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(54) Title: ORGANIC LIGHT EMITTING DEVICES HAVING CARRIER TRANSPORTING LAYERS COMPRISING METAL COMPLEXES

(57) Abstract: Light emitting devices having charge transporting layers comprising one or more metal complexes are provided. More particularly, devices include hole transporting layers comprising at least one metal complex are disclosed. The present devices can further comprise an electron blocking layer for improved efficiency.

**ORGANIC LIGHT EMITTING DEVICES HAVING CARRIER
TRANSPORTING LAYERS COMPRISING METAL COMPLEXES**

CROSS REFERENCE TO RELATED APPLICATIONS

5 This application claims the benefit of Provisional Application No. 60/315,527, filed August 29, 2001, and Application No. 60/317,541, filed September 5, 2001. This application is related to copending Provisional Application No. 60/317,540, filed on the same date, which is incorporated herein by reference in its entirety.

10 **GOVERNMENT RIGHTS**

 The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of Contract No. _____ awarded by DARPA.

15 **FIELD OF THE INVENTION**

 The present invention is directed to light emitting devices incorporating metal complexes for improved efficiency and stability.

BACKGROUND OF THE INVENTION

20 Electronic display currently is a primary means for rapid delivery of information. Television sets, computer monitors, instrument display panels, calculators, printers, wireless

phones, handheld computers, etc. aptly illustrate the speed, versatility, and interactivity that is characteristic of this medium. Of the known electronic display technologies, organic light emitting devices (OLEDs) are of considerable interest for their potential role in the development of full color, flat-panel display systems that may render obsolete the bulky cathode ray tubes still currently used in many television sets and computer monitors.

5 Generally, OLEDs are comprised of several organic layers in which at least one of the layers can be made to electroluminesce by applying a voltage across the device (see, e.g., Tang, *et al.*, *Appl. Phys. Lett.* **1987**, *51*, 913 and Burroughes, *et al.*, *Nature*, **1990**, *347*, 359). When a voltage is applied across a device, the cathode effectively reduces the adjacent organic layers (i.e., injects electrons) whereas the anode effectively oxidizes the adjacent 10 organic layers (i.e., injects holes). Holes and electrons migrate across the device toward their respective oppositely charged electrodes. When a hole and electron meet on the same molecule, recombination is said to occur and an exciton is formed. Recombination of the hole and electron is preferably accompanied by radiative emission, thereby producing electroluminescence.

15 Depending on the spin states of the hole and electron, the exciton which results from hole and electron recombination can have either a triplet or singlet spin state. Luminescence from a singlet exciton results in fluorescence whereas luminescence from a triplet exciton results in phosphorescence. Statistically, for organic materials typically used in OLEDs, about one quarter of the excitons are singlets and the remaining three quarters are triplets 20 (see, e.g., Baldo, *et al.*, *Phys. Rev. B*, **1999**, *60*, 14422). Until the discovery that there were certain phosphorescent materials that could be used to fabricate practical electro-phosphorescent OLEDs having a theoretical quantum efficiency of up to 100% (i.e., harvesting all of both triplets and singlets), the most efficient OLEDs were typically based 25 on materials that fluoresced. These materials fluoresced with a maximum theoretical quantum efficiency of only 25% (where quantum efficiency of an OLED refers to the efficiency with which holes and electrons recombine to produce luminescence), since the triplets to ground state transition is formally a spin forbidden process. Electro-phosphorescent OLEDs have now been shown to have superior overall device efficiencies as compared with electro-fluorescent OLEDs (see, e.g., Baldo, *et al.*, *Nature*, **1998**, *395*, 151 30 and Baldo, *e.g.*, *Appl. Phys. Lett.* **1999**, *75*(3), 4).

Typically, OLEDs contain several thin organic layers between a hole injecting anode layer, comprising an oxide material such as indium-tin oxide (ITO), Zn-In-SnO₂, SbO₂, or the like, and an electron injecting cathode layer, comprising a metal layer such as Mg, Mg:Ag, or LiF:Al. An organic layer residing in proximity to the anode layer is usually referred to as the "hole transporting layer" (HTL) due to its propensity for conducting positive charge (i.e., holes). Various compounds have been used as HTL materials. The most common materials consist of various triaryl amines which show high hole mobilities. Similarly, the organic layer residing in proximity to the cathode layer is referred to as the "electron transporting layer" (ETL) due to its propensity to conduct negative charge (i.e., electrons). There is somewhat more variety in the ETL materials used in OLEDs as compared with for the HTL. A common ETL material is aluminum tris(8-hydroxyquinolate) (Alq₃). Collectively, the ETL and HTL are often referred to as carrier layers. In some cases, an additional a layer may be present for enhancing hole or electron injection from the electrodes into the HTL or ETL, respectively. These layers are often referred to as hole injecting layers (HILs) or electron injecting layer (EIL). The HIL may be comprised of a small molecule such as 4,4',4''-tris(30methylphenylphenylamino)triphenylamine (MTDATA) or polymeric material such as poly(3,4-ethylenedioxythiophene) (PEDOT). The EIL may be comprised of a small molecule material such as, e.g., copper phthalocyanine (CuPc). Many OLEDs further comprise an emissive layer (EL), or alternatively termed, luminescent layer, situated between the ETL and HTL, where electroluminescence occurs. Doping of the luminescent layer with various luminescent materials has allowed fabrication of OLEDs having a wide variety of colors.

In addition to the electrodes, carrier layers, and luminescent layer, OLEDs have also been constructed with one or more blocking layers to help maximize efficiency. These layers serve to block the migration of holes, electrons, and/or excitons from entering inactive regions of the device. For example, a blocking layer that confines holes to the luminescent layer effectively increases the probability that holes will result in a photoemissive event. Hole blocking layers desirably have a deep (i.e., low) HOMO energy level (characteristic of materials that are difficult to oxidize) and conversely, electron blocking materials generally have a high LUMO energy level. Exciton blocking materials have also been shown to increase device efficiencies. Triplet excitons, which are relatively long-lived, are capable of

migrating about 1500 to 2000 Å, which is sometimes greater than the entire width of the device. An exciton blocking layer, comprising materials that are characterized by a wide band gap, can serve to block loss of excitons to non-emissive regions of the device.

In seeking greater efficiencies, devices have been experimentally created with layers containing light emitting metal complexes. Functional OLEDs having emissive layers of tris(2,2'-bipyridine)ruthenium(II) complexes or polymer derivatives thereof have been reported in Gao, *et al.*, *J. Am. Chem. Soc.*, 2000, 122, 7426, Wu, *et al.*, *J. Am. Chem. Soc.* 1999, 121, 4883, Lyons, *et al.*, *J. Am. Chem. Soc.* 1998, 120, 12100, Elliot, *et al.*, *J. Am. Chem. Soc.* 1998, 120, 6781, and Maness, *et al.*, *J. Am. Chem. Soc.* 1997, 119, 3987. Iridium-based and other metal-containing emitters have been reported in, e.g., Baldo, *et al.*, *Nature*, 1998, 395, 151; Baldo, *et al.*, *Appl. Phys. Lett.*, 1999, 75, 4; Adachi, *et al.*, *Appl. Phys. Lett.*, 2000, 77, 904; Adachi, *et al.*, *Appl. Phys. Lett.*, 2001, 78, 1622; Adachi, *et al.*, *Bull. Am. Phys. Soc.* 2001, 46, 863, Wang, *et al.*, *Appl. Phys. Lett.*, 2001, 79, 449, and U.S. Pat. Nos. 6,030,715; 6,045,930; and 6,048,630. Emissive layers containing (5-hydroxy)quinoxaline metal complexes as host material has also been described in U.S. Pat. No. 5,861,219. Efficient multicolor devices and displays are also described in U.S. Pat. No. 5,294, 870 and International Application Publication No. WO 98/06242.

A metal-containing blocking layer has also been reported. Specifically, (1,1'-biphenyl)-4-olato)bis(2-methyl-8-quinolinolato N1,O8)aluminum (BAIq) has been used as a blocking layer in the OLEDs reported in Watanabe, *et al.* "Optimization of driving lifetime durability in organic LED devices using Ir complex," in *Organic Light Emitting Materials and Devices IV*, Kafafi, ed. Proceedings of SPIE Vol.4105, p. 175 (2001).

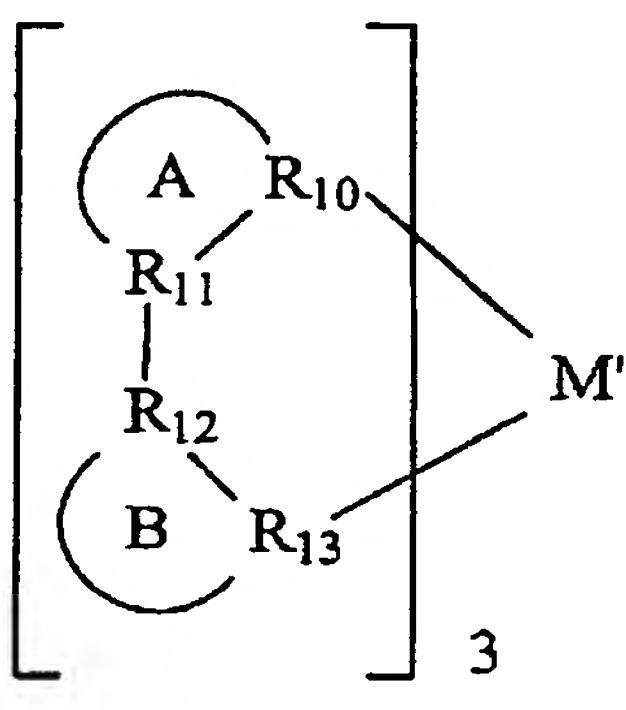
Although OLEDs promise new technologies in electronic display, they often suffer from degradation, short life spans, and loss of efficiency over time. The organic layers can be irreversibly damaged by sustained exposure to the high temperatures typically encountered in devices. Multiple oxidation and reduction events can also cause damage to the organic layers. Consequently, there is a need for the development of new materials for the fabrication of OLEDs. Compounds that are stable to both oxidation and reduction, have high T_g values, and readily form glassy thin films are desirable. The invention described hereinbelow helps fulfill these and other needs.

SUMMARY OF THE INVENTION

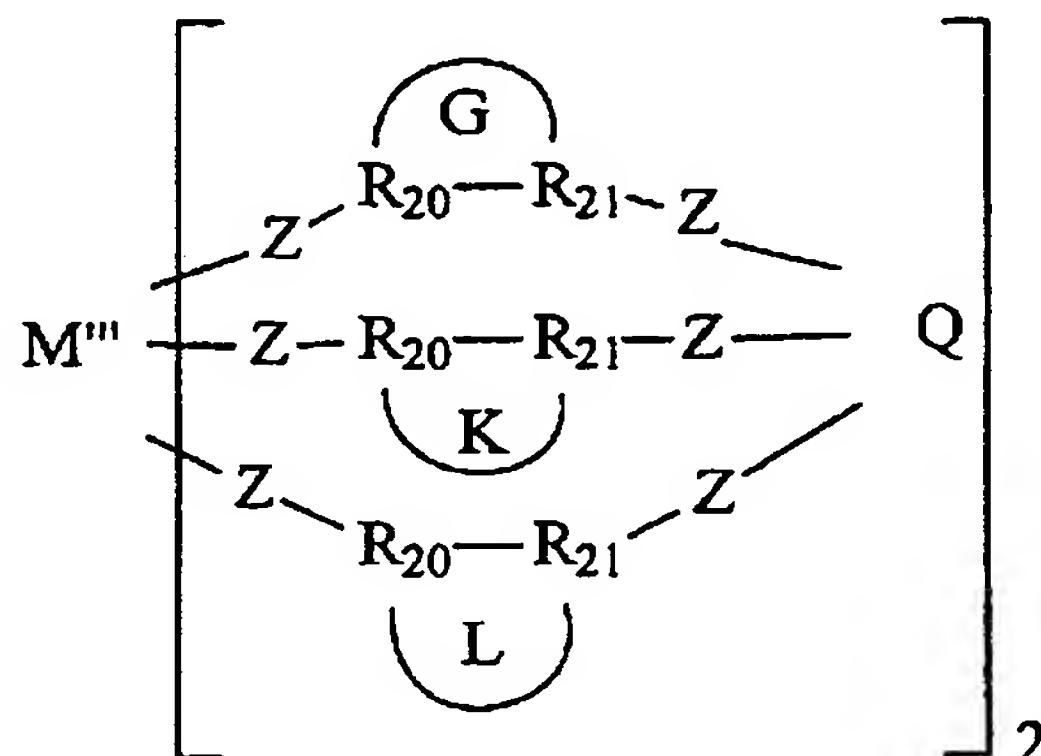
The present invention provides light emitting devices comprising a hole transporting layer that includes at least one metal complex. In some embodiments, the hole transporting layer consists essentially of said metal complex or complexes. In further embodiments, the hole transporting layer comprises an organic matrix doped with said metal complex or complexes.

In some embodiments, the metal complex is coordinatively saturated, preferably wherein metal complex has a coordination number of four or six. In some embodiments, the metal the said metal complex is a transition metal, which can be a first row, second row or third row transition metal. In some embodiments, the metal of said metal complex is Fe, Co, Ru, Pd, Os or Ir, or any subcombination thereof.

In some embodiments of the light emitting devices of the invention, at least one metal complex has one of the formulas I or II:



I



II

wherein:

M' and M''' are each, independently, a metal atom;
 R_{10} , R_{13} , R_{20} and R_2 , are each, independently, N or CH;
 R_{11} and R_{12} are each, independently, N, CH, O or S;

Ring systems A, B, G, K and L are each independently a mono-, di- or tricyclic fused aliphatic or aromatic ring system optionally containing up to 5 hetero atoms;

Z is C₁-C₆ alkyl, C₂-C₈ mono- or poly alkenyl, C₂-C₈ mono- or poly alkynyl, or a bond; and

Q is BH, N, or CH.

5. In some embodiments where the metal complex has the formula I, Ring system A and Ring system B are each monocyclic. In further embodiments where the metal complex has the formula I, Ring system A is a five membered heteroaryl monocyclic ring and Ring system B is a six membered aryl or heteroaryl monocyclic ring.

10 In some further embodiments, R₁₀ and R₁₁ are N, and R₁₃ is CH. In further embodiments, Ring A forms pyrazole. In still further embodiments, Ring B forms phenyl.

In some embodiments of the light emitting devices of the invention, the metal of at least one of the metal complexes is a d⁰, d¹, d², d³, d⁴, d⁵, or d⁶ metal. In some embodiments where the metal complex has the formula I, M' is a transition metal. In further embodiments, M' is Fe, Co, Ru, Pd, Os or Ir. In further embodiments, M' is Fe or Co. In further 15 embodiments, M' Fe, and in still further embodiments, M' is Co.

In some embodiments of the light emitting devices of the invention where the metal complex has the formula I, the metal complex is Co(ppz)₃.

20 In some embodiments of the light emitting devices of the invention, at least one metal complex has the formula II. In some embodiments of the light emitting devices of the invention where at least one metal complex has the formula II, Ring systems G, K and L are each 5 or 6 member monocyclic rings. In further embodiments, the Ring systems G, K and L are each 5-membered heteroaryl monocyclic rings. In still further embodiments, R₂₁ and R₂₂ are each N.

25 In further embodiments of the light emitting devices of the invention where at least one metal complex has the formula II, Ring systems G, K and L each form pyrazole. In further embodiments, M''' is a d^{5/6} or d^{2/3} metal.

30 In some embodiments of the light emitting devices of the invention where at least one metal complex has the formula II, M''' is a transition metal. In further embodiments, M''' is Fe, Co, Ru, Pd, Os or Ir. In further embodiments, M''' is Fe or Co. In further embodiments, M''' is Fe.

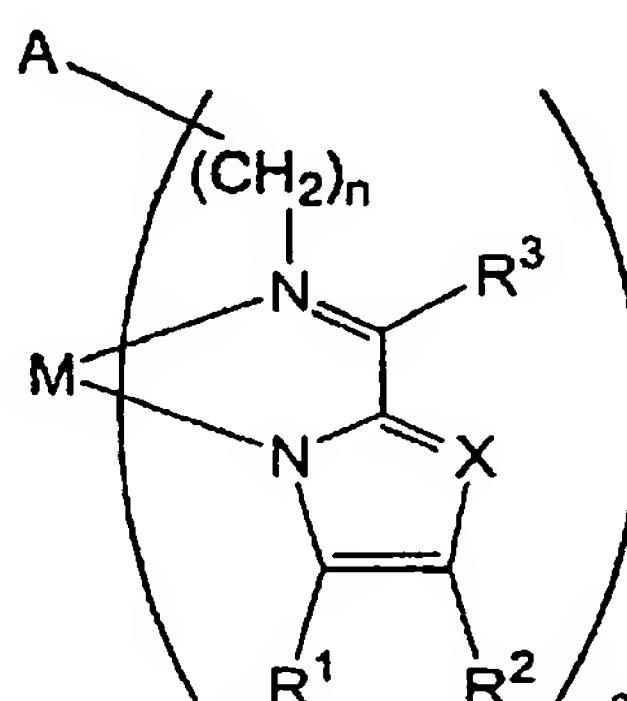
In some embodiments, the metal complex is FeTp'₂.

In some embodiments of the light emitting devices of the invention, the light emitting device further comprises an electron blocking layer, which can be include an organic electron blocking material, a metal complex, or both. In some embodiments, the organic electron blocking material is selected from triarylamines or benzidenes. In some embodiments, the 5 electron blocking layer consists essentially of the metal complex. In further embodiments, the electron blocking layer comprises a matrix doped with said metal complex.

In some embodiments, the electron blocking layer has a HOMO energy level close to the HOMO energy level of said hole transporting layer. In further embodiments, the electron blocking layer has a HOMO energy level higher than the HOMO energy level of 10 said hole transporting layer.

In some embodiments, the metal complex of the electron blocking layer comprises a metal selected from Ga, In, Sn, or a group 8, 9, or 10 transition metal. In some embodiments, the metal complex of said electron blocking layer comprises Ga. In further embodiments, the metal complex of the electron blocking layer comprises a multidentate 15 ligand. In some embodiments, the multidentate ligand has a bridging atom selected from N and P. In further embodiments, the multidentate ligand has a mesityl bridge moiety. In further embodiments, the multidentate ligand comprises up to three mono-, bi- or tricyclic heteroaromatic moieties.

In some embodiments, the of the light emitting devices of the invention, the electron 20 blocking layer comprises a compound having the formula III:



III

25 wherein:

M is a metal atom;

X is N or CX' where X' is H, C₁-C₂₀ alkyl, C₂-C₄₀ mono- or poly alkenyl, C₂-C₄₀ mono- or poly alkynyl, C₃-C₈ cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, or halo;

A is CH, CX', N, P, P(=O), aryl or heteroaryl;

each R¹ and R² is, independently, H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-

5 C₈ cycloalkyl, aryl, aralkyl, or halo; or

R¹ and R², together with the carbon atoms to which they are attached, link to form a fused C₃-C₈ cycloalkyl or aryl group;

10 R³ is H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; and

n is 1 to 5.

In some embodiments where the electron blocking layer has the formula III, M is a trivalent metal atom, X is CH or N, A is N or 1,3,5-phenyl, each R¹ and R² are H, or R¹ and R², together with the carbon atoms to which they are attached, link to form a phenyl group, R³ is H; and n is 1 or 2. In further embodiments where the electron blocking layer has 15 the formula III, M is Ga.

In further embodiments, the electron blocking layer comprises Ga(pma)₃.

In some embodiments of the light emitting devices of the invention, the metal complex of said hole transporting layer is Co(ppz)₃. In further embodiments of the light emitting devices of the invention, the metal complex of said hole transporting layer is FeTp'₂.

20 In further embodiments of the light emitting devices of the invention, the electron blocking layer comprises Ga(pma)₃ and the metal complex of said hole transporting layer is Co(ppz)₃.

In further embodiments of the light emitting devices of the invention, the electron blocking layer comprises Ga(pma)₃ and the metal complex of said hole transporting layer is 25 FeTp'₂.

The present invention also provides light emitting devices comprising the substructure HTL/EL or HTL/EBL/EL; wherein each of said EL, HTL, and EBL comprise at least one metal complex.

Also provided by the present invention are light emitting devices comprising the 30 substructure HTL/EL or HTL/EBL/EL; wherein none of said EL, HTL, or EBL is comprised

solely of organic molecules.

The present invention further provides light emitting devices having a plurality of layers, the devices being devoid of a layer that is composed solely of organic molecules. In some embodiments, each of said layers contains at least one metal complex.

The present invention also provides light emitting devices comprising a hole transporting layer, an emissive layer, and a blocking layer;

said hole transporting layer having a first HOMO energy, wherein said hole transporting layer comprises at least one metal complex;

said emissive layer comprising at least one material capable of transporting electrons, said material having a second HOMO energy; and

10 said blocking layer comprising a material having a HOMO energy that is between said first and second HOMO energies.

In some embodiments, the blocking layer resides between said hole transporting layer and said emissive layer. In further embodiments, the blocking layer comprises an organic electron blocking material, which can be, but is not necessarily, selected from triarylamines or benzidenes. In still further embodiments, electron blocking layer comprises a metal complex.

The present invention also provides methods of facilitating hole transport in a light emitting device, said light emitting device comprising a hole transporting layer and an emissive layer;

20 said hole transporting layer comprising at least one metal complex and having a first HOMO energy;

 said emissive layer comprising at least one material capable of transporting electrons, said material having a second HOMO energy higher than said HOMO energy of said hole transporting layer;

25 said method comprising the step of placing a blocking layer between said hole transporting layer and said emissive layer, wherein said blocking layer comprises a material having a HOMO energy level that is intermediate between said first and second HOMO energies.

 In some embodiments of the foregoing methods, the metal complex of said hole transporting layer is a complex formula I or II, as described above. In some embodiments,

the metal complex of the hole transporting layer is $\text{Co}(\text{ppz})_3$ or FeTp'_2 . In further embodiments, the blocking layer comprises at least one metal complex. In some embodiments, the metal complex of said blocking layer is a compound having the formula III as described above. In further embodiments, the metal complex of the blocking layer is $\text{Ga}(\text{pma})_3$. In further embodiments, the hole transporting layer comprises $\text{Co}(\text{ppz})_3$ or FeTp'_2 , and said barrier layer comprises $\text{Ga}(\text{pma})_3$.

The present invention also provides methods of fabricating a light emitting device, said method comprising placing a hole transporting layer in electrical contact with an emissive layer, wherein said hole transporting layer comprises a compound of formulas I or II as described above. In some embodiments, the light emitting device further comprises an electron blocking layer. In further embodiments, the electron blocking layer comprises a compound having the formula III as described above. In further embodiments, the electron blocking layer comprises $\text{Ga}(\text{pma})_3$. In further embodiments, the compound is a compound of formula I, and is $\text{Co}(\text{ppz})_3$ or FeTp'_2 . In further embodiments, the compound if $\text{Co}(\text{ppz})_3$.

The present invention also provides methods of transporting holes in a hole transporting layer of a light emitting device, wherein said hole transporting layer comprises at least one metal complex, said method comprising applying a voltage across said device.

Also provided by the present invention are pixels and displays comprising the devices described herein.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 compares plots of quantum efficiency v. current density for devices of the structure ITO/NPD(500 Å)/Alq₃(600 Å)/MgAg and ITO/Co(ppz)₃(500 Å)/Alq₃(600 Å)/MgAg.

Figure 2 compares plots of current density v. voltage for devices of the structure ITO/NPD(500 Å)/Alq₃(600 Å)/MgAg and ITO/Co(ppz)₃(500 Å)/Alq₃(600 Å)/MgAg.

Figure 3 compares plots of current density v. voltage for devices of the structure ITO/NPD(500 Å)/Alq₃(600 Å)/MgAg and ITO/Co(ppz)₃(500 Å)/Alq₃(600 Å)/MgAg.

Figure 4A-4C compares plots of quantum efficiency v. current density for devices comprising Co(ppz)₃.

Figure 5 compares plots of current density v. voltage for devices comprising Co(ppz)₃.

Figures 6A-6B show electronic spectra for Ga(pma)₃.

Figure 7 shows a current density v. voltage plot for a device having the structure ITO/Co(ppz)₃(400 Å)/Ga(pma)₃(100 Å)/Alq₃(500 Å)/MgAg(1000 Å)/Ag.

5 Figure 8 shows a luminance v. voltage plot for devices of the structure ITO/Co(ppz)₃(400 Å)/Ga(pma)₃(100 Å)/Alq₃(500 Å)/MgAg(1000 Å)/Ag.

Figure 9 shows an external quantum efficiency v. voltage plot for devices of the structure ITO/Co(ppz)₃(400 Å)/Ga(pma)₃(100 Å)/Alq₃(500 Å)/MgAg(1000 Å)/Ag.

10 Figure 10 shows an external quantum efficiency v. current density plot for devices of the structure ITO/Co(ppz)₃(400 Å)/Ga(pma)₃(100 Å)/Alq₃(500 Å)/MgAg(1000 Å)/Ag.

Figures 11A-11B show current density v. voltage and brightness v. voltage plots for devices having the structure ITO/HTL(500 Å)/CBP:Irppy(6%)(200 Å)/BCP(150 Å)Alq₃(200 Å)/LiF/Al.

15 Figures 12A-12B show quantum efficiency v. current density and emission spectrum plots for devices having the structure ITO/HTL(500 Å)/CBP:Irppy(6%)(200 Å)/BCP(150 Å)Alq₃(200 Å)/LiF/Al.

Figure 13 shows a plot of current v. voltage for devices of the structure ITO/Co(ppz)₃(400 Å)/NPD(100 Å)/Alq₃(500 Å)/Mg:Ag(1000 Å)/Ag(400 Å).

20 Figure 14 shows a plot of brightness v. voltage for devices of the structure ITO/Co(ppz)₃(400 Å)/NPD(100 Å)/Alq₃(500 Å)/Mg:Ag(1000 Å)/Ag(400 Å).

Figures 15A-15B show a plots of quantum efficiency v. voltage and quantum efficiency v. current density for devices of the structure ITO/Co(ppz)₃(400 Å)/NPD(100 Å)/Alq₃(500 Å)/Mg:Ag(1000 Å)/Ag(400 Å).

Figure 16 illustrates some hole transporting materials.

25 Figure 17 illustrates some metal complexes suitable in layers of the devices of the present invention.

Figure 18 describes aspects of carrier migration

Figure 19 shows chemical syntheses of metal complexes suitable in devices of the present invention.

Figure 20 shows absorption spectra of several Co compounds suitable in devices of the present invention.

Figure 21 shows cyclic voltammograms for Co complexes suitable in devices of the present invention.

Figure 22 illustrates properties of devices comprising Co compounds.

5 Figure 23 illustrates properties of devices comprising Co(ppz), and an NPD electron blocking layer.

Figure 24 illustrates photophysical properties of Ga(pma)₃.

Figure 25 illustrates properties of devices devoid of a purely organic layer.

Figure 26 illustrates properties of devices devoid of a purely organic layer.

10 Figure 27 compares properties of devices comprising NPD with properties of devices comprising Co and Ga metal complexes instead of NPD.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

As used herein, the terms "low" and "deep," in reference to molecular orbital energies, are used interchangeably. Lower and deeper generally describe molecular orbitals residing at a lower, or more stable, energy level. Ionization of electrons from deeper orbitals requires more energy than ionization of electrons in shallower, or higher, orbitals. Thus, although the deeper orbitals are said to be lower, they are often referred to numerically by higher numbers. For example, a molecular orbital residing at 5.5 eV is lower (deeper) than a molecular orbital residing at 2.5 eV. Similarly, the terms "shallow" and "high" in reference to orbital energy levels, refer to orbitals at less stable energies. These terms are well known to those skilled in the art.

25 As used herein, the term "adjacent," in reference to layers of light emitting devices, refers to layers having contacting sides. For example, a first layer and a second layer that are adjacent to one another describe, for example, contacting layers where one side of one layer is in contact with one side of the other layer.

As used herein, the term "gap" or "band-gap" generally refers to an energy difference, such as, for example, between a HOMO and a LUMO. A "wider gap" refers to an energy difference that is greater than for a "narrower gap" or "smaller gap." A "carrier gap" refers 30 to the energy difference between the HOMO and LUMO of a carrier.

The present invention is directed to, *inter alia*, light emitting devices comprising one or more layers that in turn comprise at least one metal complex. Devices, as such, may have higher efficiencies and higher stability as compared with devices having traditional organic blocking layers.

The light emitting devices of the present invention are typically layered structures that 5 electroluminesce when a voltage is applied across the device. Typical devices are structured so that one or more layers are sandwiched between a hole injecting anode layer and an electron injecting cathode layer. The sandwiched layers have two sides, one facing the anode and the other facing the cathode. These sides are referred to as the anode side and the cathode side, respectively. Layers are generally deposited on a substrate, such as glass, on 10 which either the anode layer or the cathode layer may reside. In some embodiments, the anode layer is in contact with the substrate. In many cases, for example when the substrate comprises a conductive or semi-conductive material, an insulating material can be inserted between the electrode layer and the substrate. Typical substrate materials, that may be rigid, flexible, transparent, or opaque, include glass, polymers, quartz, sapphire, and the like.

Hole transporting layers are placed adjacent to the anode layer to facilitate the 15 transport of electrons. In some embodiments, a hole injecting layer for enhancing hole injection, sometimes referred to as a hole injecting enhancement layer, may be placed adjacent to the anode, between the anode and the HTL. Materials suitable for the HTL include any material that is known by one skilled in the art to function as such. Suitable 20 materials are typically easy to oxidize and include triaryl amines such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)1,1'biphenyl-4,4'diamine (TPD), 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α -NPD), 4,4'-bis[N-(2-naphthyl)-N-phenyl-amino]biphenyl (β -NPD), and the like. Metal complexes may also be used in HTLs. Some suitable metal complexes are described, for example, in Application Ser. No. 60/283,814, filed April 13, 2001, which is 25 incorporated herein by reference in its entirety. Similarly, ETLs are situated adjacent to the cathode layer to facilitate transport of electrons. An electron injecting enhancement layer can optionally be placed adjacent to ETL or cathode layer. Materials suitable for the ETL include any materials known in the art to function as such. Typical ETL materials are relatively easy to reduce and can include, for example, aluminum tris(8-hydroxyquinolate) (Alq₃), 30 carbazoles, oxadiazoles, triazoles, thiophene, oligothiophene, and the like. HTL and ETL

carrier layers can have thicknesses ranging from about 100 to about 1000 Å. Since it is typically the site of exciton formation and luminescence, the EL layer is preferably somewhere between the HTL and ETL. The EL can optionally be in contact with one or both of the HTL and ETL or may be flanked by one or more blocking layers. EL materials can include, for example dye-doped Alq₃ and the like. In some embodiments, neat (un-doped) 5 films of luminescent material may be used as the emissive layer. Furthermore, layers can serve dual functions. For example, an ETL or HTL can also function as an EL.

In some embodiments according to the present invention, devices comprise at least one charge transport layer (i.e., carrier layer), such as, for example, a HTL, ETL, hole injecting layer, or electron injecting layer, that comprises at least one metal complex. The 10 carrier layer can be a thin film consisting essentially of metal complex or an organic matrix doped with metal complex. In some preferred embodiments, devices of the present invention comprise a hole blocking layer that includes at least one metal complex. Accordingly, in some embodiments, the metal complexes of the HTLs can be selected such that their HOMO energy levels will support hole transport. Thus, in some embodiments, it is preferable to 15 select metal complexes having HOMO energy levels in the range of from about 7 to 4.5 eV and LUMO energy levels in the range of from about 2 to about 4 eV.

Metal complexes that are suitable for use in devices as a charge transport layer can be selected on the basis of properties that facilitate this function. For example, a hole transporting material typically undergoes one electron oxidation. Thus, metal complexes that 20 are stable to one electron oxidation processes can be suitable as hole transporters. Similarly, metal complexes that are stable to one electron reductions can be suitable as electron transporting materials. Stable oxidation and reduction processes can be identified by electrochemical methods such as cyclic voltammetry, which is further discussed below. Another consideration is charge mobility. For example, materials having high hole 25 mobilities can generally function as good hole transporters. Charge mobility often corresponds with low reorganizational energies for redox processes. Thus, for example, metal complexes showing little structural differences when oxidized or reduced typically have a relatively small energy barrier (reorganizational energy) associated with oxidation or reduction. Certain metal properties such as electron configuration can affect reorganizational 30 barriers, as is well known in the art and further discussed below. Additionally, certain ligand

properties, such as denticity, can affect reorganizational barriers of redox events in metal complexes, the details of which are also further discussed below.

In some embodiments, it is desirable that one or more layers of the device comprise one or more dopants. Emissive dopants (i.e., photoemitting molecules, emitters) can be included in at least one layer, such as for example the EL, for improved efficiency and color tunability. Doped layers usually comprise a majority of host material and minority of dopant. Host material (also referred to as matrix) typically transfers excitons through a non-radiative process to the emissive dopant material, which then emits light of a wavelength characteristic of the dopant, rather than the host.

Dopants can also serve to trap charge. For example, the LUMO levels of the host and dopant can be arranged such that the LUMO level of the dopant is lower than the LUMO level of the host, such that the dopant molecule can act as an electron trap. Similarly, the HOMO levels of the host and dopant can be arranged such that the HOMO level of the dopant is higher than the HOMO level of the host, such that the dopant molecule would act as a hole trap. In addition, one or more dopants, referred to as transfer dopants, can be used to facilitate the transfer of energy from the host to the emissive dopant. For example, cascade doping can be used, which involves the non-radiative transfer of excitons from a molecule of the host through one or more transfer dopants to the emissive dopant. These intermediate transfers can be by Förster transfer, Dexter transfer, hole trapping or electron trapping that eventually leads to the formation of an exciton on the transfer dopant or the emissive dopant, or by any other suitable mechanism.

Dopants can be present in the host material in quantities ranging, for example, from about 0.1% to about 50%, from about 1% to about 20%, or from 1% to about 10% by weight. A level of about 1% by weight of doping is preferred for emissive dopants in host material. Alternatively, in some embodiments, levels of dopant result in an average intermolecular distance between dopant molecules of about the Förster radius of the dopant, such as, for example, from about 20 to about 40 Å, or from about 25 to about 35 Å, or about 30 Å. Emissive dopants can include any compound that is capable of photoemission. Emissive dopants include fluorescent organic dyes, such as laser dyes, as known and used in the art. Preferred emissive dopants include phosphorescent metal complexes such as the Ir, Pt, and other heavy metal complexes disclosed in Application Ser. Nos. 08/980,986, filed December 30, 1997, and U.S. Pat. No. 5,834,882, issued November 10, 1998, both of which are incorporated by reference.

1,1997,09/883,734, filed June 18, 2001, and 60/283,814, filed April 13, 2001, each of which is herein incorporated by reference in its entirety.

In some embodiments, devices of the present invention comprise at least one blocking layer. Blocking layers (BLs) function to confine holes, electrons, and/or excitons to specific regions of the light emitting devices. For example, device efficiency can be increased when excitons are confined to the EL and/or when holes and electrons are prevented from migrating out of the EL. Blocking layers can serve one or more blocking functions. For example, a hole blocking layer can also serve as an exciton blocking layer. In some embodiments, the hole blocking layer does not simultaneously serve as an emissive layer in devices of the present invention. Although a blocking layer can include compounds that are capable of emitting, emission can occur in a separate emissive layer. Thus, in preferred embodiments, the blocking layer does not luminesce. Blocking layers can be thinner than carrier layers. Typical blocking layers have thicknesses ranging from about 50 Å to about 1000 Å, or from about 50 Å to about 750 Å, or from about 50 Å to about 500 Å. Additionally, blocking layers preferably comprise compounds other than BA_{lq}.

Hole blocking layers (HBLs) are typically comprised of materials that have difficulty acquiring a hole. For example, hole blocking materials can be relatively difficult to oxidize. In most instances, hole blocking materials are more difficult to oxidize than an adjacent layer from transporting holes. A material that is more difficult to oxidize than another material typically possesses a lower HOMO energy level. For example, holes originating from the anode and migrating into an EL can be effectively blocked from exiting the EL (on the cathode side) by placing a blocking layer of material adjacent to the EL on the cathode side of the device. The blocking layer preferably has a HOMO energy level lower than the HOMO energy levels of the EL. Larger differences in HOMO energy levels correspond to better hole blocking ability. The HOMO of the materials of the blocking layer are preferably at least about 50, 100, 200, 300, 400, 500 meV (milli-electronvolts) or more deeper than the HOMO level of an adjacent layer in which holes are to be confined. In some embodiments, the HOMO of the materials of the blocking layer are at least about 200 meV deeper than the HOMO level of an adjacent layer in which holes are to be confined.

In some devices of the invention, the layer in which holes are to be confined can comprise more than one material, such as a host material (matrix) and a dopant. In this case,

a HBL preferably has a HOMO energy level that is lower (deeper) than the material of the adjacent layer which carries the majority of positive charge (i.e., the material with the highest (shallowest) HOMO energy level). For example, an emissive layer can comprise a host material having a deeper HOMO energy level than the dopant. In this case, the dopant acts as a trap for holes and can be the principle hole transporter of the emissive layer. Thus, in such embodiments, the HOMO energy of the dopant is considered when selecting a hole blocking layer. Thus, in some embodiments, the HOMO energy level of the HBL can be higher than the host material and lower than that of the dopant.

Hole blocking layers are also preferably good electron injectors. Accordingly, the LUMO energy level of the HBL is preferably close to the LUMO energy level of the layer in which holes are to be confined. Differences in LUMO energy levels between the two layers in some embodiments can be less than about 500 meV, 200 meV, 100 meV, 50 meV, or even smaller. Hole blocking layers that are also good electron injectors typically have smaller energy barriers to electron injection than for hole leakage. Accordingly, the difference between the LUMO energies of the HBL and the layer in which holes are to be confined (corresponding to an electron injection energy barrier) is smaller than the difference in their HOMO energies (i.e., hole blocking energy barrier).

Conversely, electron blocking layers (EBLs) are comprised of materials that have difficulty acquiring electrons (i.e., are relatively difficult to reduce). In the context of a light emitting device, EBLs are preferably more difficult to reduce than the adjacent layer from which electrons migrate. A material that is more difficult to reduce than another material generally has a higher LUMO energy level. As an example, electrons originating from the cathode and migrating into an EL layer can be blocked from exiting the EL (on the anode side) by placing a blocking layer adjacent to the anode side of the EL where the blocking layer has a LUMO energy level higher than the LUMO energy level of the EL. Larger differences in LUMO energy levels correspond to better electron blocking ability. The LUMO of the materials of the blocking layer are preferably at least about 50 meV, 100 meV, 200 meV, 300 meV, 400 meV, 500 meV or more higher (shallower) than the LUMO level of an adjacent layer in which holes are to be confined. In some embodiments, the LUMO of the materials of the blocking layer can be at least about 200 meV higher (shallower) than the LUMO level of an adjacent layer in which holes are to be confined.

In some embodiments, the layer in which electrons are to be confined can comprise more than one material, such as a host material (matrix) and a dopant. In this case, an EBL preferably has a LUMO energy level that is higher than the material of the adjacent layer which carries the majority of negative charge (e.g., either the host or dopant having the lowest LUMO energy level). For example, an emissive layer can include a host material having a deeper LUMO energy level than the dopant. In this case, the host can be the principle electron transporter of the emissive layer. In such embodiments, the LUMO energy level of the EBL can be higher than the host material and lower than that of the dopant. Similarly, if the dopant served as the primary carrier of electrons, then the EBL preferably has a higher LUMO than the dopant.

Electron blocking layers are also preferably good hole injectors. Accordingly, the HOMO energy level of the EBL is preferably close to the HOMO energy level of the layer in which electrons are to be confined. Differences in HOMO energy levels between the two layers in some embodiments can be less than about 500 meV, 200 meV, 100 meV, 50 meV, or even smaller. Electron blocking layers that are also good hole injectors typically have smaller energy barriers to hole injection than for electron leakage. Accordingly, the difference between the HOMO energies of the EBL and the layer in which electrons are to be confined (corresponding to an hole injection energy barrier) is smaller than the difference in their LUMO energies (i.e., electron blocking energy barrier).

Migration of excitons from the EL to other parts of the devices can be blocked with materials that have difficulty acquiring excitons. Transfer of an exciton from one material to another may be prevented when the receiving material has a wider (greater) optical gap than the exciton donating material. For example, excitons can be substantially confined to the EL layer of a device by placing, adjacent to the EL layer, an exciton blocking layer having a wider optical gap than the materials comprising the EL layer. Exciton blocking layers can also be placed on either side of the EL. Exciton blocking layers can also serve as HBLs or EBLs, depending on the energy levels of the HOMO or LUMO of the exciton blocking material compared with those of adjacent layers (as discussed above). Additionally, exciton blocking layers can be good electron or hole injectors when either the HOMO or LUMO energy level of the exciton blocking layer is close in energy to the respective HOMO or LUMO energy level of an adjacent layer. For example, in devices

having an exciton blocking layer and an emissive layer, the exciton blocking layer can have a HOMO energy level that is less than about 500, 200, or 100 meV from the HOMO energy level of said emissive layer. Conversely, the exciton blocking layer can have a LUMO energy level that is less than about 500, 200, 100 meV from the LUMO energy level of said emissive layer.

5 According to some embodiments of the present invention, blocking layers can also comprise dopants. As an example, the blocking layer can be comprised of a wide band-gap matrix (host) material doped with a smaller band-gap dopant. Depending on the matrix and dopant combination, the effective LUMO energy of the blocking layer can be lowered by the presence of dopant, consequently improving the electron conduction and injection properties
10 of a hole blocking layer. Conversely, the effective HOMO energy of the blocking layer can be raised by the presence of dopant, thereby improving hole injection properties. As an example, in some embodiments, HBLs comprise a wide band-gap matrix doped with a smaller band-gap material where the deep HOMO energy level of the matrix serves to prevent transport of holes and the relatively shallow LUMO level of the dopant favors
15 electron injection. In some embodiments of the invention, the matrix can comprise a substantially conjugated organic molecule such as, for example, octaphenyl cyclooctatetraene (OPCOT), oligophenylenes such as hexaphenyl, and other similar materials having a wide band-gap. Suitable matrix band gap values can be at least about 3 eV, but can also be at least about 2.5 eV, 3.0 eV, 3.3 eV, 3.5 eV or higher. Dopant is preferably a metal complex.
20 Doping levels can range from about 1% to about 50%, or more preferably from about 5% to about 20%, or even more preferably from about 10 to about 15% by weight. An example of a suitable metal complex used as a dopant for blocking layers is bis(2-(4,6-difluorophenyl)pyridyl-N, C2')iridium(III) picolinate (FIrpic). An example of hole blocking layer comprising a matrix doped with a metal complex is OPCOT doped with 15% by weight
25 of FIrpic (OPCOT:FIrpic(15%)). For example, OPCOT:FIrpic can effectively confine holes to an emissive layer comprising CBP doped with Ir(ppy)₃ (tris(2-phenylpyridyl-N, C2')iridium(III), Irppy) because the HOMO of OPCOT is lower than the HOMO of Irppy and the LUMO of FIrpic is higher than the LUMO of CBP.

Metal complexes used in the devices of the present invention include any metal
30 coordination complex comprising at least one metal atom and at least one ligand. Metal

complexes can be charged or uncharged; however, uncharged complexes are more amenable to the thin layer deposition techniques used in OLED fabrication. Metal complexes are preferably stable to both one electron oxidation and one electron reduction processes. Redox-stable complexes can be identified, for example, by cyclic voltammetry (e.g., identification of reversible redox events). Additionally, such metal complexes often have low reorganizational energy barriers associated with oxidation and reduction. Accordingly, complexes having low reorganizational energy barriers show little structural difference between resting state, oxidized, and reduced state. Metal complexes typically characterized as having low reorganizational energy barriers include complexes having d⁰, d¹, d², d³, d⁴, d⁵ and d⁶ electron configurations. For example, octahedral complexes having d³ or d⁶ metals typically generally have low reorganizational energy barriers. Metal complexes in which redox events affect predominantly non-bonding molecular orbitals (such as the t_{2g} set in octahedral transition metal complexes) generally have low reorganizational energy barriers, since little structural change is seen in the ligand set upon oxidation or reduction. Reorganizational energy associated with redox events can also be modulated by the ligand set. For example, multidentate ligands can structurally impose a certain coordination geometry in metal complexes. Relatively rigid tridentate, tetradentate, hexadentate ligands, and the like can constrain coordination geometry such that redox events do not result in significant structural reorganization. Additionally, metal complexes that are coordinatively saturated, such as six-coordinate complexes, which are less likely to have significant structural change associated with oxidation or reduction, are also preferred. Four-coordinate complexes can also be suitable and can include both tetrahedral and square-planar complexes as well as others. Octahedral complexes are also suitable due to their propensity for forming glassy films. Metal complexes comprising aromatic ligands may help facilitate redox processes, preferably in those instances where redox events are largely centered on the ligand. Furthermore, metal complexes comprising heavy metals are preferred over those with lighter metals for their greater thermal stability. For example, complexes comprising second and third row transition metals are preferred.

Any metal atom, in any of its accessible oxidation states, is suitable in metal complexes, including main group, transition metals, lanthanides, actinides, alkaline earth, and alkali metals. Transition metals include Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb,

Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg. Main group metals include Al, Ga, Ge, In, Sn, Sb, Tl, Pb, Bi, and Po. In some embodiments, metals having an atomic number greater than about 13, 36, or 54 are preferred.

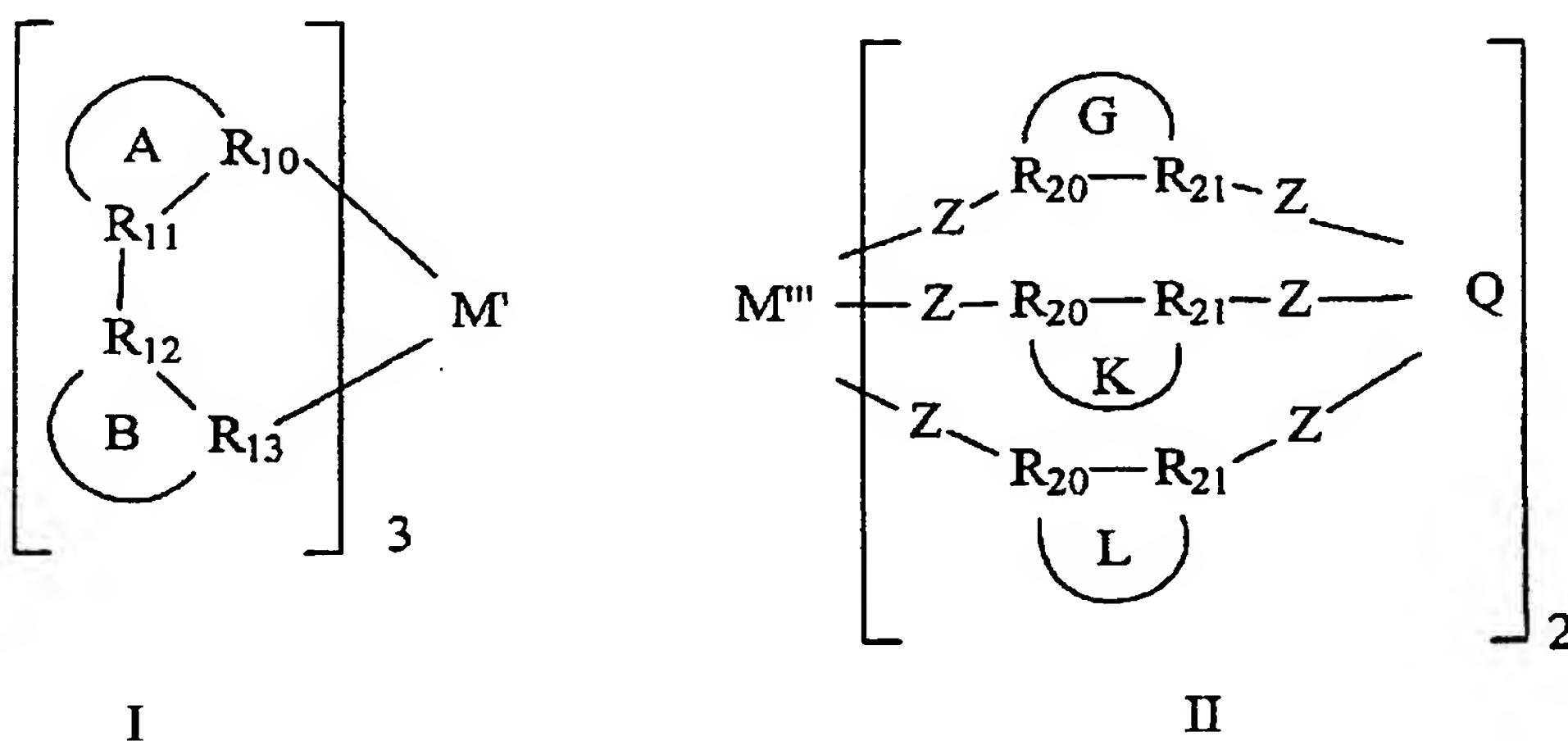
Metal complexes can include any suitable ligand system. Suitable ligands can be monodentate, bidentate, multidentate, π -bonding, organic, inorganic, charged, or uncharged.

5 Further, ligands preferably comprise one or more heteroatoms through which the metal atom is coordinated, although organometallic compounds comprising coordinating carbon are also suitable and also considered as metal complexes. Coordinating heteroatoms of the ligands can include oxygen, nitrogen, sulphur, phosphorus, and the like. Nitrogen-containing ligands can include amines, nitrenes, azide, diazenes, triazenes, nitric oxide, polypyrazolylborates, 10 heterocycles such as 2,2'-bipyridine (bpy), 1,10-phenanthroline, terpyridine (trpy), pyridazine, pyrimidine, purine, pyrazine, pyridine, 1,8-naphthyridine, pyrazolate, imidazolate, and macrocycles including those with and without a conjugated π system, and the like. Phosphorus-containing ligands typically include phosphines and the like. Oxygen-containing ligands include water, hydroxide, oxo, superoxide, peroxide, alkoxides, alcohols, aryloxides, 15 ethers, ketones, esters, carboxylates, crown ethers, β -diketones, carbamate, dimethylsulfoxide, and oxo anions such as carbonate, nitrate, nitrite, sulfate, sulfite, phosphate, perchlorate, molybdate, tungstate, oxalate and related groups. Sulfur-containing ligands can include hydrogen sulfide, thiols, thiolates, sulfides, disulfides, thioether, sulfur oxides, dithiocarbamates, 1,2-dithiolenes, and the like. Ligands comprising coordinating carbon atoms can include cyanide, carbon disulfide, alkyl, alkenes, alkynes, carbide, cyclopentadienide, and the like. Halides can also serve as ligands. Metal complexes containing these and other ligands are described in detail in Cotton and Wilkinson, *Advanced Inorganic Chemistry*, Fourth Ed., John Wiley & Sons, New York, 1980, which is incorporated herein by reference in its entirety. Additional suitable ligands are described in 20 Application Ser. Nos. 60/283,814, filed April 13, 2001 and 09/883,734, filed June 18, 2001, each of which is incorporated herein by reference in its entirety.

Ligands, especially neutral ligands, can be further derivatized with one or more substituents, including anionic groups, to fully or partially neutralize any positive formal charge associated with the metal atoms of the metal complexes. Suitable anionic substituents can include carbonate, nitrate, nitrite, sulfate, sulfite, phosphate, and the like.

Examples of suitable metal complexes for use in hole transporting layers can include, *inter alia*, transition metal complexes having first, second, or third row transition metals, including, for example, Fe, Co, Ru, Pd, Os, and Ir. Further examples include coordinatively saturated complexes and complexes that are six- or four-coordinate.

In some embodiments of the present invention, devices comprise a hole blocking layer comprising at least one metal complex of Formula I or II:



10 wherein:

M' and M''' are each, independently, a metal atom;

R₁₀, R₁₃, R₂₀ and R₂₁ are each, independently, N or CH;

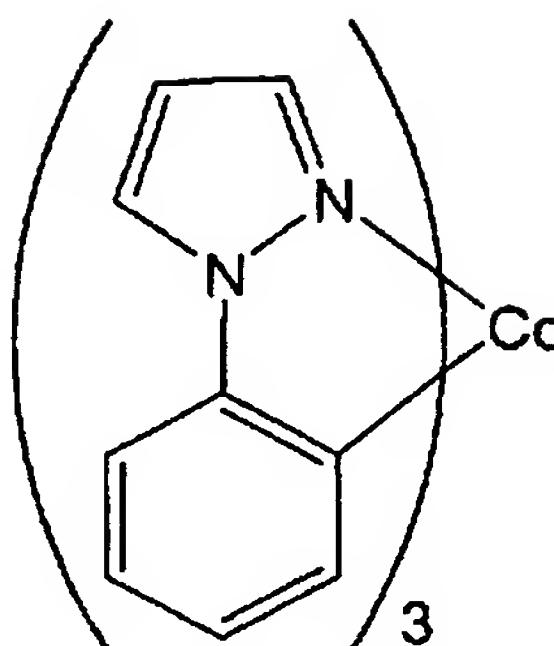
R₁₁ and R₁₂ are each, independently, N, CH, O or S;

15 Ring systems A, B, G, K and L are each independently a mono-, di- or tricyclic fused aliphatic or aromatic ring system optionally containing up to 5 hetero atoms;

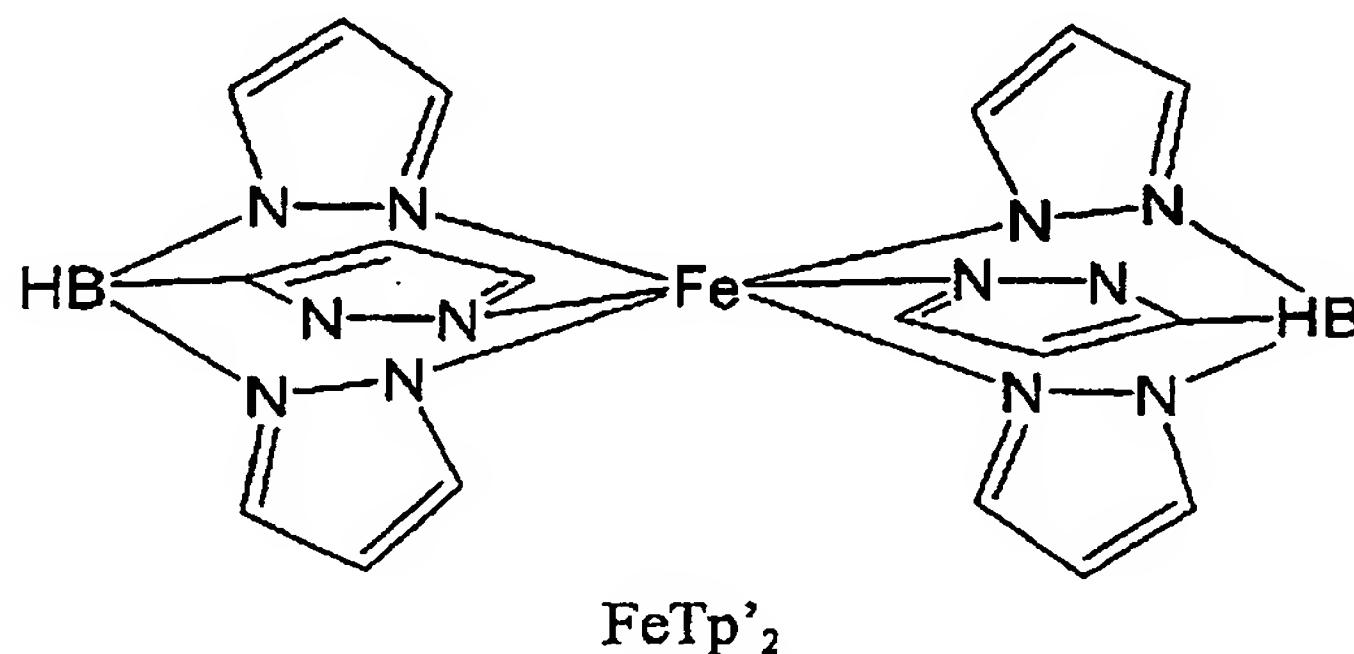
Z is C₁-C₆ alkyl, C₂-C₈ mono- or poly alkenyl, C₂-C₈ mono- or poly alkynyl, or a bond; and

Q is BH, N, or CH.

A particularly suitable compound of the above Formula I is Co(ppz)₃, the structure 20 of which is shown below.

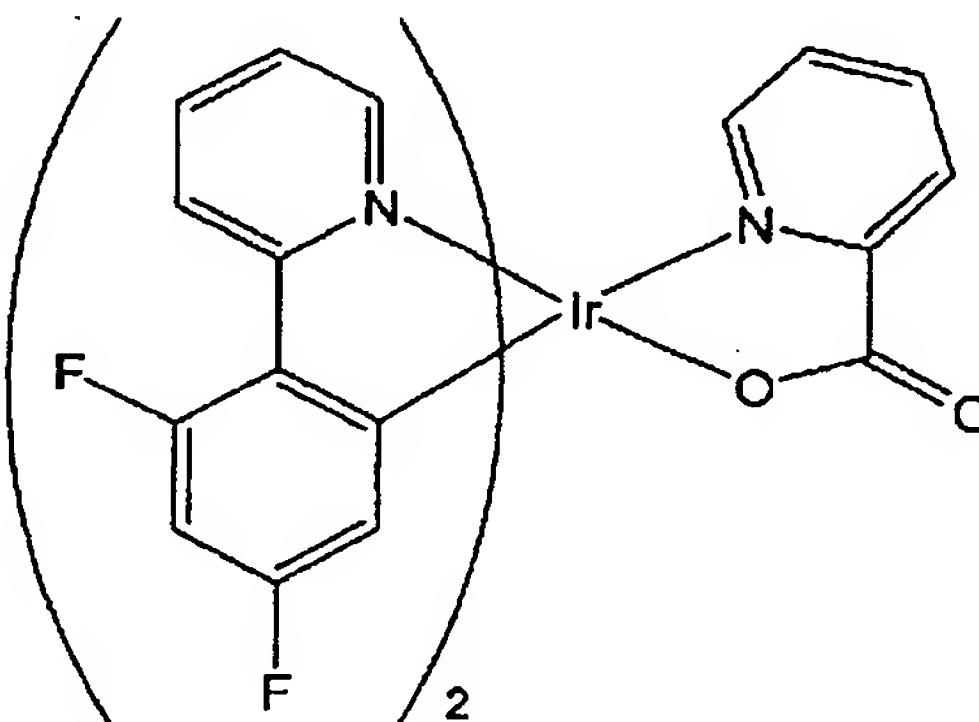
 $\text{Co}(\text{ppz})_3$

Another particularly suitable compound of the above Formula II is iron trispyrazolylborate (FeTp'_2), the structure of which is shown below.

 FeTp'_2

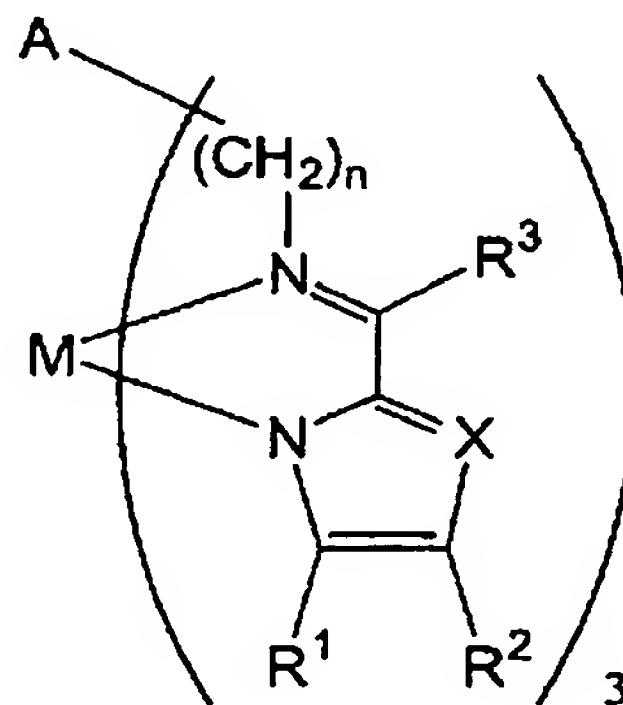
Metal complexes suitable for hole blocking layers can include, *inter alia*, complexes of Os, Ir, Pt, and Au, including those described in Application Ser. Nos. 08/980,986, filed December 1, 1997, 09/883,734, filed June 18, 2001, and 60/283,814, filed April 13, 2001, each of which is herein incorporated by reference in its entirety. An example of a metal complex suitable in hole blocking layers is bis(2-(4,6-disfluorophenyl)pyridyl-N, C2')iridium(III) picolinate (FIrpic), the structure of which is shown below.

15



bis(2-(4,6-difluorophenyl)pyridyl-N, C2')iridium(III) picolinate (FIrpic)

Metal complexes suitable for electron blocking layers include those that are relatively difficult to reduce (i.e., high LUMO energy level). Suitable metal complexes include metal complexes of the formula:



M is a metal atom;

X is N or CX' where X' is H, C₁-C₂₀ alkyl, C₂-C₄₀ mono- or poly alkenyl, C₂-C₄₀ 10 mono- or poly alkynyl, C₃-C₈ cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, or halo;

A is CH, CX', N, P, P(=O), aryl or heteroaryl;

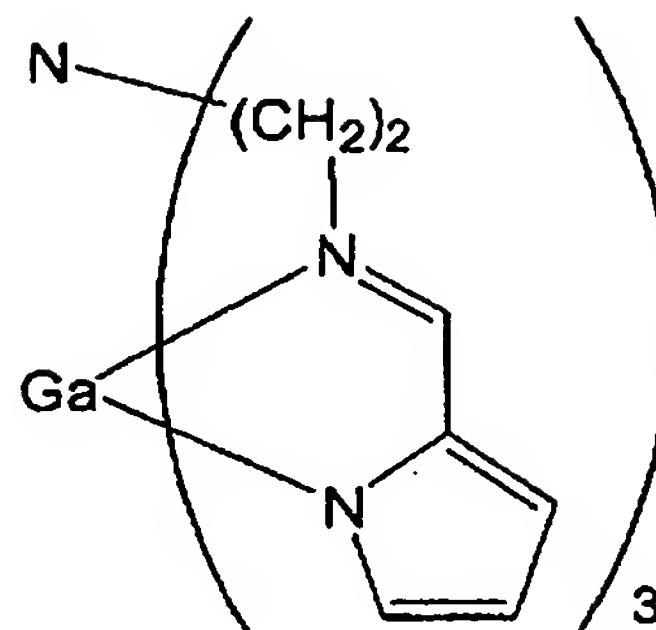
each R¹ and R² is, independently, H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; or

R¹ and R², together with the carbon atoms to which they are attached, link to form 15 a fused C₃-C₈ cycloalkyl or aryl group;

R³ is H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; and

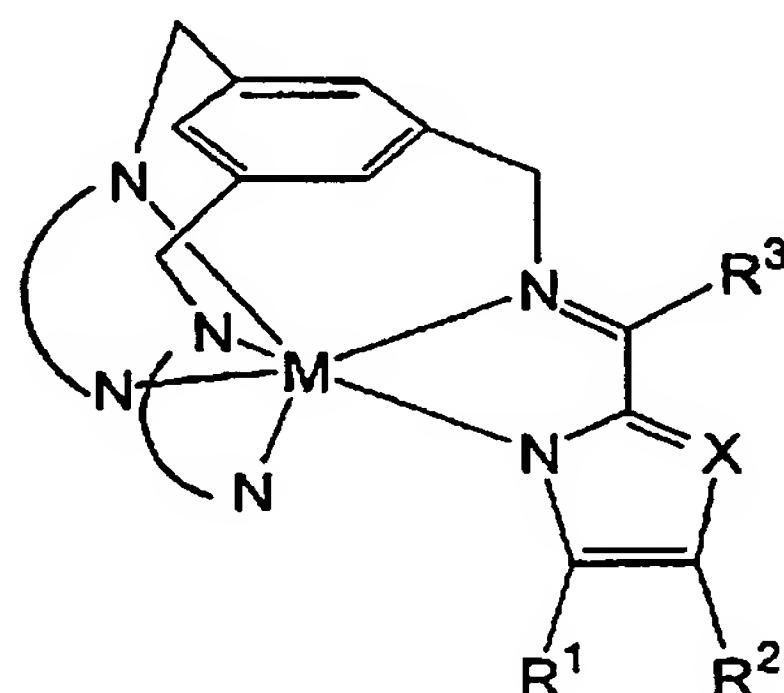
n is 1 to 5.

In some preferred embodiments, M is a trivalent metal such as Al or Ga. Variable A 20 may preferably be CR³ or N. R¹ and R², in some embodiments, join to form a fused aromatic ring such as phenyl or pyridyl. A particularly suitable compound of the above formula is gallium(III)tris[2-(((pyrrole-2-yl)methylidene)amino)ethyl]amine (Ga(pma)₃) shown below.



Other suitable metal complexes may have the formula

5



wherein:

- M is a metal atom;
- is N or CX' where X' is H, C₁-C₂₀ alkyl, C₂-C₄₀ mono- or poly alkenyl, C₂-C₄₀ mono- or poly alkynyl, C₃-C₈ cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, or halo;
- 10 each R¹ and R² is, independently, H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; or
- R¹ and R², together with the carbon atoms to which they are attached, link to form a fused C₃-C₈ cycloalkyl or aryl group; and
- 15 R³ is H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo.

As referred to throughout the present disclosure, alkyl groups include optionally substituted linear and branched aliphatic groups. Cycloalkyl refers to cyclic alkyl groups, including, for example, cyclohexyl and cyclopentyl, as well as heterocycloalkyl groups such as pyranyl, and furanyl groups. Cycloalkyl groups may be optionally substituted. Alkenyl groups may be substituted or unsubstituted and comprise at least one carbon-carbon double

bond. Alkynyl groups may be substituted or unsubstituted and comprise at least one carbon-carbon triple bond. Aryl groups are aromatic and substituted aromatic groups having about 3 to about 50 carbon atoms, including, for example, phenyl and naphthyl. Heteroaryl groups are aromatic or substituted aromatic groups having from about 3 to about 50 carbon atoms and comprising at least one heteroatom. Examples of heteroaryl groups include pyridyl and imidazolyl groups. Aralkyl groups can be substituted or unsubstituted and have about 3 to about 30 carbon atoms, and include, for example, benzyl. Heteroaralkyl include aralkyl groups comprising at least one hetero atom. Halo includes fluoro, chloro, bromo, and iodo. Substituted groups may contain one or more substituents. Suitable substituents may include, for example, H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, C₃-C₈ 5 heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halo, amino, azido, nitro, carboxyl, cyano, aldehyde, alkylcarbonyl, aminocarbonyl, hydroxyl, alkoxy, and the like. Substituents can also be electron-withdrawing groups and electron-donating groups. As used herein, the term "hetero" is intended to denote a non-carbon atom, for example N, O, or S.

Metal complexes suitable for exciton blocking layers include those that have relatively wide optical gaps. Metal complexes suitable for the preparation of hole blocking layers include high energy absorbers and emitters, such as for example, blue emitters. Preferred metal complexes include those in which the metal has a closed valence shell (no unpaired electrons). As a result, many preferred metal complexes for preparing exciton blocking layers are colorless, since their optical gap energy falls outside the visible range. Further, complexes having heavy metals are preferred. For example, heavy metals of the second and third row transition series tend to have larger optical gaps due to a stronger ligand field. Examples of suitable metal complexes for exciton blocking layers include, *inter alia*, complexes of Os, Ir, Pt, and Au, such as those described in Application Ser. Nos. 08/980,986, filed December 1, 1997, 09/883,734, filed June 18, 2001, and 60/283,814, filed April 13, 10 20 25 2001, each of which is herein incorporated by reference in its entirety. In some embodiments, metal complexes suitable for exciton blocking layers include FIrpic, Ga(pma)₃, and related compounds.

According to some embodiments of the present invention, devices can include a hole transporting layer that includes at least one metal complex, and, in some embodiments, an electron blocking layer that includes, for example, organic material, a metal complex, or

both. Suitable organic materials include any organic electron blocking material known in the art such as, for example, triarylaminos or benzidines. In some embodiments, the electron blocking layer resides between the HTL and EL. Accordingly, the electron blocking layer can be selected such that the HOMO energy level of the electron blocking layer falls between the HOMO energy levels of the HTL and EL. In other embodiments, the HOMO energy level of the electron blocking layer is close to the HOMO energy level of the hole transporting layer. For example, the magnitude of the difference between the HOMO energy levels of the electron blocking layer and the hole transporting layer can be about 500, 200, 100, 50 meV or less. Examples of metal complexes suitable as electron blocking layers include complexes having Ga, In, Sn or a transition metal such as a group 8, 9, or 10 transition metal. Other examples of suitable metal complexes include complexes having multidentate ligands. A particularly suitable metal complex is Ga(pma)₃.

While the metal complexes of the metal complex-containing HTLs described herein can impart charge-carrying and/or blocking functions, the metal complexes also provide the additional advantage of increasing the thermal stability of devices of the invention. This is significant because OLEDs and similar light emitting devices can be subject to elevated temperatures for prolonged periods of time, and such exposure is thought to be a limiting factor in the lifetimes of such devices. Accordingly, devices of the invention containing for example, complexes of heavy metals such as second and third row transition metals and fourth and fifth row main group metals are envisaged to benefit in terms of lifetime of the device.

The HOMO and LUMO energy levels for OLED materials, can be measured, or estimated, in several ways known in the art. The two common methods for estimating HOMO energy levels include solution electrochemistry, such as cyclic voltammetry, and ultraviolet photoelectron spectroscopy (UPS). Two methods for estimating LUMO levels include solution electrochemistry and inverse photoemission spectroscopy. As discussed above, alignment of the HOMO and LUMO energy levels of adjacent layers can control the passage of holes and electrons between the two layers.

Cyclic voltammetry is one of the most common methods for determining oxidation and reduction potentials of compounds. This technique is well known to those skilled in the art, and a simple description of this process follows. A test compound is dissolved along

with a high concentration of electrolyte. Electrodes are inserted and the voltage scanned in either the positive or negative direction (depending on whether an oxidation or reduction is being performed). The presence of a redox reaction is indicated by current flowing through the cell. The voltage scan is then reversed and the redox reaction is reversed. The reference can be an external electrode, such as Ag/AgCl or SCE, or it can be an internal one, such as 5 ferrocene, which has a known oxidation potential. The latter is often preferred for organic solvents, since the common reference electrodes are water based. A useful parameter that may come from cyclic voltammetry is the carrier gap. If both the reduction and oxidation are reversible, one can determine the energy difference between the hole and the electron (i.e. taking an electron out of the HOMO versus putting one into the LUMO). This value can be 10 used to determine the LUMO energy from a well defined HOMO energy. Method for determining redox potentials and reversiblity of redox events using cyclic voltammetry is well known in the art.

UPS is an alternative technique for determining absolute binding energies in the solid state. Although solution electrochemistry is typically adequate for most compounds, and for 15 giving relative redox potentials, the measurements taken in the solution phase can differ from values in the solid phase. A preferred method of estimating HOMO energies in the solid state is UPS. This is a photoelectric measurement, where the solid is irradiated with UV photons. The energy of the photons are gradually increased until photogenerated electrons are observed. The onset of ejected electrons gives the energy of the HOMO. The photons at that energy have just enough energy to eject an electron from the top of the filled levels. 20 UPS provides HOMO energy level values in eV relative to vacuum which corresponds to the binding energy for the electron.

Inverse photoemission may be used to directly estimate LUMO energy levels. This technique involves pre-reducing the sample and then probing the filled states to estimate the 25 LUMO energies. More specifically, a material is injected with electrons which then decay into unoccupied states and emit light. By varying the energy of the incoming electrons and the angle of the incident beam, electronic structure of a material can be studied. Methods of measuring LUMO energy levels using inverse photoemission are well known to those skilled in the art.

30 Optical gap values can be determined from the intersection of the normalized

absorption and emission spectra. For molecules that have very little structural rearrangement in going from the ground state to the excited, such that the gap between the absorption and emission λ_{max} values is rather small, the intersection energy is a good estimate of the optical gap (the 0-0 transition energy). Thus, the optical gap roughly corresponds to the HOMO-LUMO gap, and such estimation may be adequate for ideal systems. However, if the shift
5 between the absorption and emission maxima is large (Stokes shift) the optical gap can be more difficult to determine. For example, if there is a structural rearrangement in the excited state or the measured absorption does not represent the lowest energy excited state, then there can be a substantial error. Thus, for the selection of potential exciton blocking materials, the edge of the absorption band of the material is preferably used to obtain a value for its optical
10 gap. In this way, device layers comprising materials having absorption band energies higher than for adjacent layers may serve as effective exciton blocking layers. For example, if an exciton approaches a layer in a device having a higher energy absorption edge than the material containing the exciton, the probability that the exciton will be transferred into the higher energy material is low. For molecules emitting from triplet excited states, the
15 absorption edge is a preferred estimate for optical gap, since the intersystem crossing leads to a very large Stokes shift.

Light emitting devices of the present invention can be fabricated by a variety of techniques well known to those skilled in the art. Small molecule layers, including those comprised of neutral metal complexes, can be prepared by vacuum deposition, organic vapor
20 phase deposition (OVPD), such as disclosed in Application No. 08/972,156, filed November 17, 1997, which is incorporated herein by reference in its entirety, or solution processing such as spin coating. Polymeric films can be deposited by spin coating and CVD. Layers of charged compounds, such as salts of charged metal complexes, can be prepared by solution methods such as spin coating or by an OVPD method such as disclosed in U.S. Pat.
25 No. 5,554,220, which is incorporated herein by reference in its entirety. Layer deposition generally, though not necessarily, proceeds in the direction of the anode to the cathode, and the anode typically rests on a substrate. As such, methods of fabricating devices, involving depositing a blocking layer that comprises a metal complex onto a preexisting layer, are also encompassed by the present invention. Preexisting layers include any layer that is designed
30 to be in contact with the blocking layer. In some embodiments, the preexisting layer can be

an emissive layer or a HTL. Devices and techniques for their fabrication are described throughout the literature and in, for example, U.S. Pat. Nos. 5,703,436; 5,986,401; 6,013,982; 6,097,147; and 6,166,489. For devices from which light emission is directed substantially out of the bottom of the device (i.e., substrate side), a transparent anode material such as ITO may be used as the bottom electrode. Since the top electrode of such a device does not need to be transparent, such a top electrode, which is typically a cathode, may be comprised of a thick and reflective metal layer having a high electrical conductivity. In contrast, for transparent or top-emitting devices, a transparent cathode may be used such as disclosed in U.S. Pat. Nos. 5,703,436 and 5,707,745, each of which is incorporated herein by reference in its entirety. Top-emitting devices may have an opaque and/or reflective substrate, such that light is produced substantially out of the top of the device. Devices can also be fully transparent, emitting from both top and bottom.

Transparent cathodes, such as those used in top-emitting devices preferably have optical transmission characteristics such that the device has an optical transmission of at least about 50%, although lower optical transmissions can be used. In some embodiments, devices include transparent cathodes having optical characteristics that permit the devices to have optical transmissions of at least about 70%, 85%, or more. Transparent cathodes, such as those described in U.S. Pat. Nos. 5,703,436 and 5,707,745, typically comprise a thin layer of metal such as Mg:Ag with a thickness, for example, that is less than about 100 Å. The Mg:Ag layer can be coated with a transparent, electrically-conductive, sputter-deposited, ITO layer. Such cathodes are often referred to as compound cathodes or as TOLED (transparent-OLED) cathodes. The thickness of the Mg:Ag and ITO layers in compound cathodes may each be adjusted to produce the desired combination of both high optical transmission and high electrical conductivity, for example, an electrical conductivity as reflected by an overall cathode resistivity of about 30 to 100 ohms per square. However, even though such a relatively low resistivity can be acceptable for certain types of applications, such a resistivity can still be somewhat too high for passive matrix array OLED pixels in which the current that powers each pixel needs to be conducted across the entire array through the narrow strips of the compound cathode.

The present invention further includes methods of facilitating hole transport in a light emitting device, wherein the light emitting device preferably comprises a hole transporting layer and an emissive layer, and wherein the hole transporting layer comprises at least one metal complex. In accordance with preferred embodiments of the methods, the device is designed such that the emissive layer has a higher HOMO energy level than the HOMO energy level of the hole transporting layer. In some embodiments, the methods involve placing an electron blocking layer between the HTL and EL, where the HOMO energy level of the electron blocking layer has a HOMO energy level between that of the HTL and EL.

5 The present invention further includes methods of transporting holes in a hole transporting layer of a light emitting device, where said hole transporting layer comprises at least one metal complex, comprising applying a voltage across a device of this structure.

10 Structures of light emitting devices are often referred to by a sequential listing of layer materials separated by slashes. For example, a device having an anode layer adjacent to a hole transporting which is adjacent to an emissive layer which is adjacent to an electron blocking layer which is adjacent to a cathode layer can be written as anode/HTL/EL/ETL/cathode. As such, devices of the present invention can include the substructures HTL/EL/HBL, HTL/EBL/EL, HTL/EBL/ETL, and others. Some preferred structures of the present invention include anode/HTL/EL/HBL/ETL/cathode and anode/HTL/EBL/EL/ETL/cathode. Other embodiments include devices with substructures HTL/EL or HTL/EBL/EL where each of the EL, HTL, and EBL comprise at least one metal 15 complex or where none of the EL, HTL, or EBL comprise solely organic molecules. Further embodiments include a device, having a plurality of layers, devoid of a layer that is composed solely of organic molecules or a device having a plurality of layers where each of the layers contains at least one metal complex.

15 Light emitting devices of the present invention can be used in a pixel for a display. Virtually any type of display can incorporate the present devices. Displays can include computer monitors, televisions, personal digital assistants, printers, instrument panels, bill boards, and the like. In particular, the present devices can be used in heads-up displays because they can be substantially transparent when not in use.

20 As those skilled in the art will appreciate, numerous changes and modifications can be made to the preferred embodiments of the invention without departing from the spirit of

the invention. It is intended that all such variations fall within the scope of the invention.

Throughout this specification various groupings are employed to conveniently describe constituent variables of compounds and groups of various related moieties. It is specifically intended that each occurrence of such groups throughout this specification include every possible subcombination of the members of the groups, including the individual members thereof.

It is intended that each of the patents, applications, and printed publications mentioned in this patent document be hereby incorporated by reference in their entirety.

EXAMPLES

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Example 1: Synthesis of *Tris* (1-phenylpyrazole-C²,N') cobalt (III) (Co(ppz)₃)

To a solution of 1-phenylpyrazole (1.0 equiv. Mol, 6.93 mmol), in THF (3 ml), was added ethylmagnesium bromide (1.1 equiv. Mol, 7.6mmol). The reaction mixture was refluxed for three hours under argon atmosphere, and then cooled in a dry ice/acetone bath. 15 A solution of cobalt (II) bromide (0.5 equiv mol, 3.47mmol) in THF (8ml) was then added slowly to the Grignard. Immediately the reaction mixture turned black. The bath was removed and the mixture was stirred two days.

The reaction mixture was transferred to a separatory funnel containing aqueous NH₄Cl (10g/liter, 75ml) and CH₂Cl₂ (75ml) and shook. The resulting thick emulsion was 20 passed through a course fritted funnel, which aided the separation of the two layers. The organic layer was isolated and the aqueous layer was extracted twice more with CH₂Cl₂ (75ml). The CH₂Cl₂ solutions were combined, dried over MgSO₄, filtered and concentrate under reduced pressure. Addition of hexanes to the black/yellow concentrate caused the product to precipitate as a dark yellow solid. ¹H NMR analysis indicated that the crude 25 product was a mixture of facial and meridonal isomers, as well as a small amount of impurities. An attempt was made to separate the two isomers and impurities by column chromatography, using silica gel and 1:1 CH₂Cl₂: toluene eluent. Only the facial isomer exited the column, whereas the meridonal isomer stuck to the silica and soon after turned purple in color.

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Example 2: Synthesis of *Tris* (1-(4-tolylphenyl)pyrazole-C²,N') cobalt (III) (CoMPPZ)

Ligand synthesis (4-tolylphenylpyrazole): A 250ml flask was charged with a magnetic stirrer bar, 4-tolylboronic acid (16mmol, 2.0equiv.), pyrazole (8mmol, 1.0equiv.), anhydrous cupric acetate (12mmol, 1.5mmol), 6g activated 4Å molecular sieves, pyridine (16mmol, 2.0equiv.), and 96 ml dichloromethane. The reaction was stirred under air at ambient temperature in a loosely capped flask for 2 days. The reaction mixture was filtered through Celite, washed with water and purified by silica gel chromatography (eluent: ethyl acetate: hexane=1:7)

Complex synthesis: To a solution of 4-tolylpyrazole (1.0 equiv. Mol, 6.93mmol), in THF (3ml), was added ethylmagnesium bromide (1.1 equiv. Mol, 7.6mmol). The reaction mixture was refluxed for three hours under argon atmosphere, and then cooled in a dry ice/acetone bath. A solution of cobalt (II) bromide (0.5 equiv mol, 3.47mmol) in THF (8ml) was then added slowly to the Grignard. Immediately the reaction mixture turned black. The bath was removed and the mixture was stirred two days.

The reaction mixture was transferred to a separatory funnel containing aqueous NH₄Cl (10g/liter, 75ml) and CH₂Cl₂ (75ml) and shook. The resulting thick emulsion was passed through a course fritted funnel, which aided the separation of the two layers. The organic layer was isolated and the aqueous layer was extracted twice more with CH₂Cl₂ (75ml). The CH₂Cl₂ solutions were combined, dried over MgSO₄, filtered and concentrate under reduced pressure. Addition of hexanes to the black/yellow concentrate caused the product to precipitate as a dark yellow solid. ¹H NMR analysis indicated that the crude product was a mixture of facial and meridonal isomers, as well as a small amount of impurities. An attempt was made to separate the two isomers and impurities by column chromatography, using silica gel and 1:1 CH₂Cl₂: toluene eluent. Only the facial isomer exited the column, whereas the meridonal isomer stuck to the silica and soon after turned purple in color.

Example 3: Synthesis of *Tris* (1-(4-methoxyphenyl)pyrazole-C²,N') cobalt (III) (CoMOPPZ)

Ligand synthesis (4-methoxyphenylpyrazole): A 250ml flask was charged with a magnetic stirrer bar, 4-methoxyboronic acid (16mmol, 2.0equiv.), pyrazole (8mmol,

1.0equiv.), anhydrous cupric acetate (12mmol, 1.5mmol), 6g activated 4Å molecular sieves, pyridine (16mmol, 2.0equiv.), and 96 ml dichloromethane. The reaction was stirred under air at ambient temperature in a loosely capped flask for 2 days. The reaction mixture was filtered through Celite, washed with water and purified by silica gel chromatography (eluent: ethyl acetate: hexane=1:7)

5 Complex synthesis: To a solution of 4-methoxypyrazole (1.0 equiv. Mol, 6.93mmol), in THF (3ml), was added ethylmagnesium bromide (1.1 equiv. Mol, 7.6mmol). The reaction mixture was refluxed for three hours under argon atmosphere, and then cooled in a dry ice/acetone bath. A solution of cobalt (II) bromide (0.5 equiv mol, 3.47mmol) in THF (8ml) was then added slowly to the Grignard. Immediately the reaction mixture turned
10 black. The bath was removed and the mixture was stirred two days.

The reaction mixture was transferred to a separatory funnel containing aqueous NH₄Cl (10g/liter, 75ml) and CH₂Cl₂ (75ml) and shook. The resulting thick emulsion was passed through a course fritted funnel, which aided the separation of the two layers. The organic layer was isolated and the aqueous layer was extracted twice more with CH₂Cl₂
15 (75ml). The CH₂Cl₂ solutions were combined, dried over MgSO₄, filtered and concentrate under reduced pressure. Addition of hexanes to the black/yellow concentrate caused the product to precipitate as a dark yellow solid. ¹H NMR analysis indicated that the crude product was a mixture of facial and meridonal isomers, as well as a small amount of impurities. An attempt was made to separate the two isomers and impurities by column
20 chromatography, using silica gel and 1:1 CH₂Cl₂: toluene eluent. Only the facial isomer exited the column, whereas the meridonal isomer stuck to the silica and soon after turned purple in color.

**Example 4: Synthesis of *Tris* (1-(4,5-difluorophenyl)pyrazole-C²,N') cobalt (III)
25 (CodFPPZ)**

Ligand synthesis (4,5-difluorophenylpyrazole): A 250ml flask was charged with a magnetic stirrer bar, 4,5-difluoroboronic acid (16mmol, 2.0equiv.), pyrazole (8mmol, 1.0equiv.), anhydrous cupric acetate (12mmol, 1.5mmol), 6g activated 4Å molecular sieves, pyridine (16mmol, 2.0equiv.), and 96 ml dichloromethane. The reaction was stirred under air at ambient temperature in a loosely capped flask for 2 days. The reaction mixture was
30

filtered through Celite, washed with water and purified by silica gel chromatography (eluent: ethyl acetate: hexane=1:7)

Complex synthesis: To a solution of 4,5-difluoropyrazole (1.0 equiv. Mol, 6.93mmol), in THF (3ml), was added ethylmagnesium bromide (1.1 equiv. Mol, 7.6mmol). The reaction mixture was refluxed for three hours under argon atmosphere, and then cooled 5 in a dry ice/acetone bath. A solution of cobalt (II) bromide (0.5 equiv mol, 3.47mmol) in THF (8ml) was then added slowly to the Grignard. Immediately the reaction mixture turned black. The bath was removed and the mixture was stirred two days.

The reaction mixture was transferred to a separatory funnel containing aqueous NH₄Cl (10g/liter, 75ml) and CH₂Cl₂ (75ml) and shook. The resulting thick emulsion was 10 passed through a coarse fritted funnel, which aided the separation of the two layers. The organic layer was isolated and the aqueous layer was extracted twice more with CH₂Cl₂ (75ml). The CH₂Cl₂ solutions were combined, dried over MgSO₄, filtered and concentrate under reduced pressure. Addition of hexanes to the black/yellow concentrate caused the 15 product to precipitate as a dark yellow solid. ¹H NMR analysis indicated that the crude product was a mixture of facial and meridonal isomers, as well as a small amount of impurities. An attempt was made to separate the two isomers and impurities by column chromatography, using silica gel and 1:1 CH₂Cl₂: toluene eluent. Only the facial isomer exited the column, whereas the meridonal isomer stuck to the silica and soon after turned purple in color.

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Example 5: Synthesis of *Tris* (1-(4-fluorophenyl)pyrazole-C²,N') cobalt(III) (CoFPPZ)

Ligand synthesis (4-fluorophenylpyrazole): A 250ml flask was charged with a magnetic stirrer bar, 4-fluoroboronic acid (16mmol, 2.0equiv.), pyrazole (8mmol, 1.0equiv.), anhydrous cupric acetate (12mmol, 1.5mmol), 6g activated 4Å molecular sieves, pyridine 25 (16mmol, 2.0equiv.), and 96 ml dichloromethane. The reaction was stirred under air at ambient temperature in a loosely capped flask for 2 days. The reaction mixture was filtered through Celite, washed with water and purified by silica gel chromatography (eluent: ethyl acetate: hexane=1:7)

Complex synthesis: To a solution of 4-fluoropyrazole (1.0 equiv. Mol, 6.93mmol), in THF (3ml), was added ethylmagnesium bromide (1.1 equiv. Mol, 7.6mmol).

The reaction mixture was refluxed for three hours under argon atmosphere, and then cooled in a dry ice/acetone bath. A solution of cobalt (II) bromide (0.5 equiv mol, 3.47mmol) in THF (8ml) was then added slowly to the Grignard. Immediately the reaction mixture turned black. The bath was removed and the mixture was stirred two days.

The reaction mixture was transferred to a separatory funnel containing aqueous
5 NH₄Cl (10g/liter, 75ml) and CH₂Cl₂ (75ml) and shook. The resulting thick emulsion was passed through a course fritted funnel, which aided the separation of the two layers. The organic layer was isolated and the aqueous layer was extracted twice more with CH₂Cl₂ (75ml). The CH₂Cl₂ solutions were combined, dried over MgSO₄, filtered and concentrate under reduced pressure. Addition of hexanes to the black/yellow concentrate caused the
10 product to precipitate as a dark yellow solid. ¹H NMR analysis indicated that the crude product was a mixture of facial and meridonal isomers, as well as a small amount of impurities. An attempt was made to separate the two isomers and impurities by column chromatography, using silica gel and 1:1 CH₂Cl₂: toluene eluent. Only the facial isomer exited the column, whereas the meridonal isomer stuck to the silica and soon after turned
15 purple in color.

**Example 6: Synthesis of *Tris* (1-(4-*tert*-butylphenyl)pyrazole-C²,N') cobalt (III)
(CoBPPZ)**

Ligand synthesis (4-*tert*-phenylpyrazole): A 250ml flask was charged with a
20 magnetic stirrer bar, 4-*tert*-boronic acid (16mmol, 2.0equiv.), pyrazole (8mmol, 1.0equiv.), anhydrous cupric acetate (12mmol, 1.5mmol), 6g activated 4Å molecular sieves, pyridine (16mmol, 2.0equiv.), and 96 ml dichloromethane. The reaction was stirred under air at ambient temperature in a loosely capped flask for 2 days. The reaction mixture was filtered through Celite, washed with water and purified by silica gel chromatography (eluent: ethyl acetate: hexane=1:7)

Complex synthesis: To a solution of 4-*tert*-pyrazole (1.0 equiv. Mol, 6.93mmol), in THF (3ml), was added ethylmagnesium bromide (1.1 equiv. Mol, 7.6mmol). The reaction mixture was refluxed for three hours under argon atmosphere, and then cooled in a dry ice/acetone bath. A solution of cobalt (II) bromide (0.5 equiv mol, 3.47mmol) in THF (8ml)

was then added slowly to the Grignard. Immediately the reaction mixture turned black. The bath was removed and the mixture was stirred two days.

The reaction mixture was transferred to a separatory funnel containing aqueous NH₄Cl (10g/liter, 75ml) and CH₂Cl₂ (75ml) and shook. The resulting thick emulsion was passed through a coarse fritted funnel, which aided the separation of the two layers. The 5 organic layer was isolated and the aqueous layer was extracted twice more with CH₂Cl₂ (75ml). The CH₂Cl₂ solutions were combined, dried over MgSO₄, filtered and concentrate under reduced pressure. Addition of hexanes to the black/yellow concentrate caused the product to precipitate as a dark yellow solid. ¹H NMR analysis indicated that the crude product was a mixture of facial and meridonal isomers, as well as a small amount of 10 impurities. An attempt was made to separate the two isomers and impurities by column chromatography, using silica gel and 1:1 CH₂Cl₂: toluene eluent. Only the facial isomer exited the column, whereas the meridonal isomer stuck to the silica and soon after turned purple in color.

15 **Example 7: Synthesis of Ga(III)tris[2-((pyrrole-2-yl)methylidene)amino]ethyl]amine (Ga(pma)₃)**

The ligand [((pyrrole-2-yl)methylidene)amino]ethyl]amine was prepared by adding a methanolic solution of pyrrole-2-carboxaldehyde (1.430 g, 15 mmol, 100 mL) to a methanolic solution of tris(2-aminoethyl)amine (0.720 g, 5 mmol, 10 mL). The resulting 20 yellow solution was stirred at room temperature for 30 min. A methanolic solution of gallium(III) nitrate hydrate (1.280 g, 5 mmol, 150 mL) was added to the ligand solution and stirred at room temperature for 30 min. The solution was filtered and left to stand at ambient temperature until crystallization occurred. The crude material was then sublimed at 235 °C.

25 **Example 8: Devices of the present invention.**

Functional OLEDs were prepared with the structure ITO/HTL/Alq₃/MgAg where Co(ppz)₃ was used as the HTL. These devices had lower efficiency than for comparable devices in which the HTL was composed of triarylamines. Higher efficiencies were achieved for these devices when a thin layer of NPD was inset between the Co(ppz)₃ and Alq₃ layers.

The HOMO levels for both NPD and Co(ppz)₃ are at comparable energies (5.5 eV for NPD and 5.4 eV for Co(ppz)₃). See Figures 13-15.

Example 9: Devices according to embodiments of the present invention.

Functional OLEDs were prepared with a Co(ppz)₃ hole transporting layer, a Ga(pma)₃ electron blocking layer and an Alq₃ emissive layer. The turn on voltage was roughly 3.5 V (voltage at which external brightness = Cd/m²), and the peak efficiency was greater than 1.2%. See Figures 7-10.

Example 10: Devices according to embodiments of the present invention

Functional OLEDs were prepared with a Co(ppz)₃/Ga(pma)₃ hole tranporting layer and a doped CBP emissive layer. An analogous device was also prepared with an NPD hole transporting layer. Overall, the Co(ppz)₃/(Ga(pma)₃) device performed better than the device with the NPD layer. The low voltage currents are lower and the spectra show no blue emission (below 400 nm) for Co(ppz)₃/(Ga(pma)₃). The turn-on voltages for the Co(ppz)₃/(Ga(pma)₃) based device was slightly higher than for the NPD-based device and the quantum efficiency was lower. Both of these parameters are expected to improve with device optimization. See Figures 11-12.

20

25

What is claimed is:

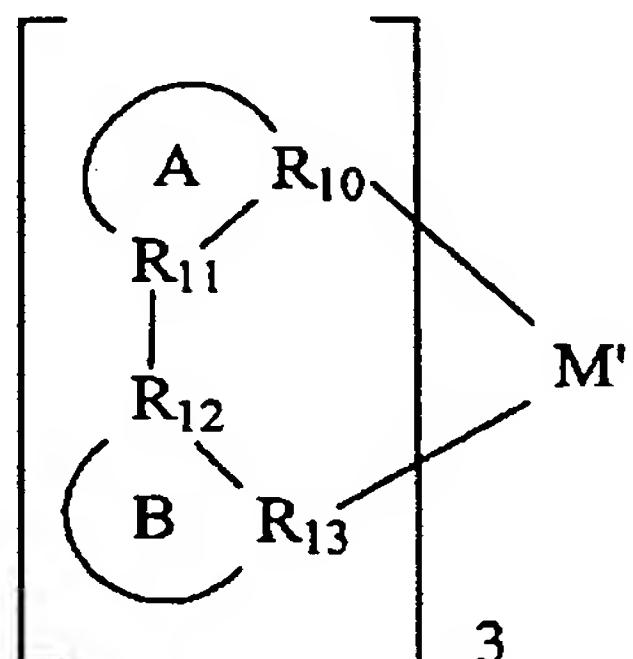
1. A light emitting device comprising a hole transporting layer, wherein said hole transporting layer comprises at least one metal complex.
2. The light emitting device of claim 1 wherein said hole transporting layer consists essentially of said metal complex.
3. The light emitting device of claim 1 wherein said hole transporting layer comprises an organic matrix doped with said metal complex.
4. The light emitting device of claim 1 wherein said metal complex is coordinatively saturated.
5. The light emitting device of claim 1 wherein said metal complex has a coordination number of six.
6. The light emitting device of claim 1 wherein said metal complex has a coordination number of four.
7. The light emitting device of claim 1 wherein said metal of said metal complex is a transition metal.
8. The light emitting device of claim 7 wherein said transition metal is a first row transition metal.
9. The light emitting device of claim 7 wherein said transition metal is a second or third row transition metal.
10. The light emitting device of claim 1 wherein the metal of said metal complex is Fe, Co, Ru, Pd, Os or Ir.

11. The light emitting device of claim 1 wherein the metal of said metal complex is Fe or Co.

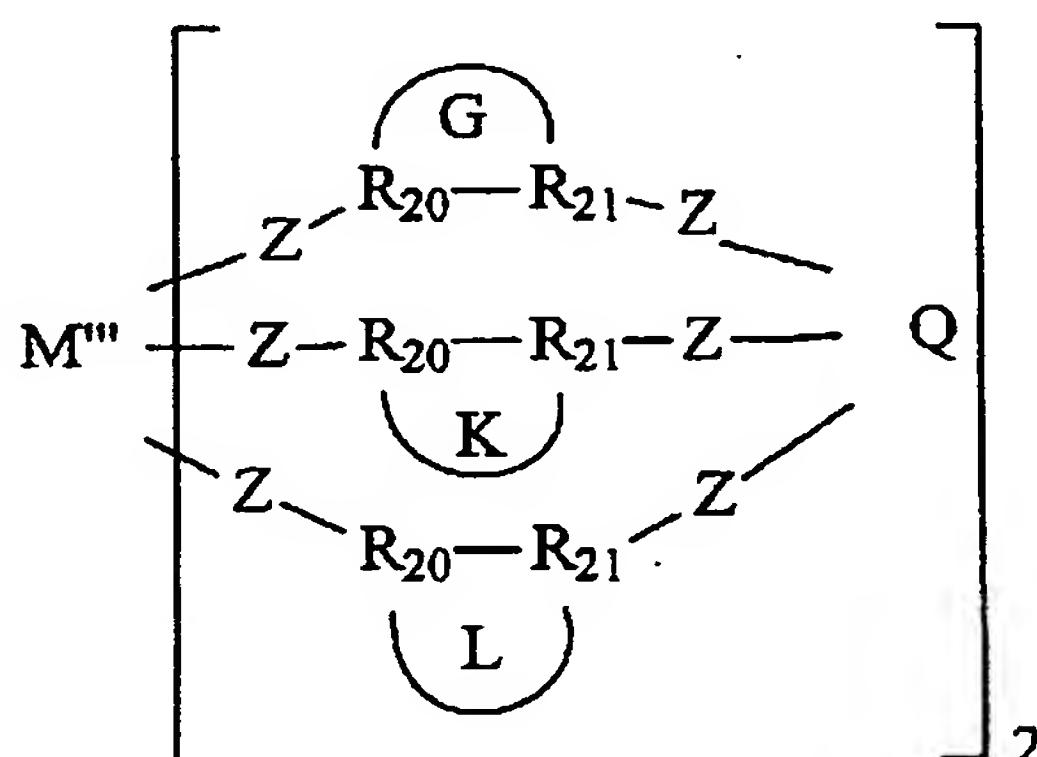
12. The light emitting device of claim 1 wherein the metal of said metal complex is Fe.

13. The light emitting device of claim 1 wherein the metal of said metal complex is Co.

14. The light emitting device of claim 1 wherein said metal complex has one of the formulas I or II:



I



II

wherein:

M' and M''' are each, independently, a metal atom;

R₁₀, R₁₃, R₂₀ and R₂₁ are each, independently, N or CH;

R₁₁ and R₁₂ are each, independently, N, CH, O or S;

Ring systems A, B, G, K and L are each independently a mono-, di- or tricyclic fused aliphatic or aromatic ring system optionally containing up to 5 hetero atoms;

Z is C₁-C₆ alkyl, C₂-C₈ mono- or poly alkenyl, C₂-C₈ mono- or poly alkynyl, or a bond; and

Q is BH, N, or CH.

15. The light emitting device of claim 14 wherein said metal complex has the formula I.
16. The light emitting device of claim 15 wherein said metal complex has the formula I and wherein Ring system A and Ring system B are each monocyclic.
17. The light emitting device of claim 16 wherein said metal complex has the formula I, Ring system A is a five membered heteroaryl monocyclic ring and Ring system B is a six membered aryl or heteroaryl monocyclic ring.
18. The light emitting device of claim 17 wherein R₁₀ and R₁₁ are N, and R₁₃ is CH.
19. The light emitting device of claim 17 wherein Ring A forms pyrazole.
20. The light emitting device of claim 17 wherein Ring B forms phenyl.
21. The light emitting device of claim 14 wherein said metal is a d⁰, d¹, d², d³, d⁴, d⁵, or d⁶ metal.
22. The light emitting device of claim 14 wherein M' is a transition metal.
23. The light emitting device of claim 14 wherein M' is Fe, Co, Ru, Pd, Os or Ir.
24. The light emitting device of claim 14 wherein M' is Fe or Co.
25. The light emitting device of claim 14 wherein M' is Co.
26. The light emitting device of claim 14 wherein M' is Fe.

27. The light emitting device of claim 1 wherein said metal complex is $\text{Co}(\text{ppz})_3$.
28. The light emitting device of claim 14 wherein said metal complex has the formula II.
29. The light emitting device of claim 14 wherein said metal atom complex has the formula II and wherein Ring systems G, K and L are each 5 or 6 member monocyclic rings.
30. The light emitting device of claim 29 wherein Ring systems G, K and L are each 5-membered heteroaryl monocyclic rings.
31. The light emitting device of claim 30 wherein R_{21} and R_{22} are each N.
32. The light emitting device of claim 31 wherein ring systems G, K and L each form pyrazole.
33. The light emitting device of claim 28 wherein M''' is a $d^{5/6}$ or $d^{2/3}$ metal.
34. The light emitting device of claim 28 wherein M''' is a transition metal.
35. The light emitting device of claim 28 wherein M''' is Fe, Co, Ru, Pd, Os or Ir.
36. The light emitting device of claim 28 wherein M''' is Fe or Co.
37. The light emitting device of claim 14 wherein M''' is Fe.
38. The light emitting device of claim 1 wherein said metal complex is FeTp'_2 .

39. The light emitting device of claim 1 further comprising an electron blocking layer.

40. The light emitting device of claim 39 wherein said electron blocking layer comprises an organic electron blocking material.

41. The light emitting device of claim 40 wherein said organic electron blocking material is selected from triarylamines or benzidenes.

42. The light emitting device of claim 39 wherein said electron blocking layer comprises a metal complex.

43. The light emitting device of claim 42 wherein said electron blocking layer consists essentially of said metal complex.

44. The light emitting device of claim 42 wherein said electron blocking layer comprises a matrix doped with said metal complex.

45. The light emitting device of claim 42 wherein said electron blocking layer has a HOMO energy level close to the HOMO energy level of said hole transporting layer.

46. The light emitting device of claim 42 wherein said electron blocking layer has a HOMO energy level higher than the HOMO energy level of said hole transporting layer.

47. The light emitting device of claim 42 wherein said metal complex of said electron blocking layer comprises a metal selected from Ga, In, Sn, or a group 8, 9, or 10 transition metal.

48. The light emitting device of claim 42 wherein said metal complex of said electron blocking layer comprises Ga.

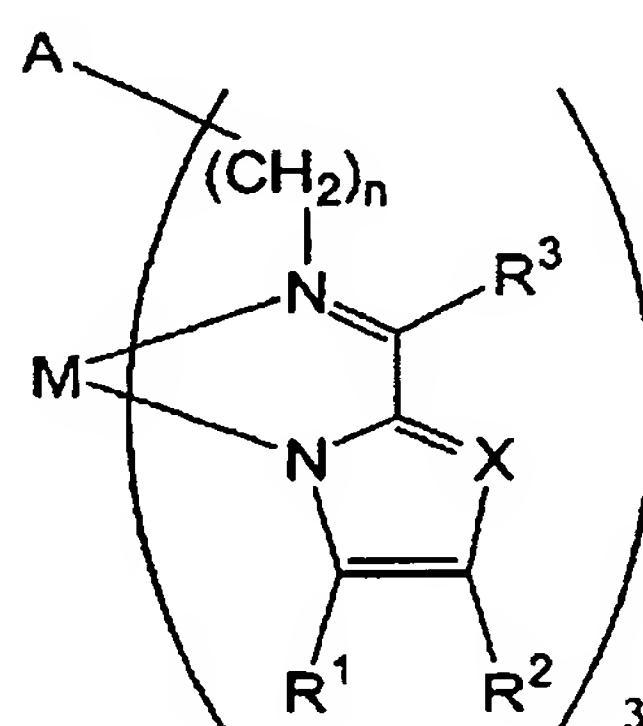
49. The light emitting device of claim 42 wherein said metal complex of said electron blocking layer comprises a multidentate ligand.

50. The light emitting device of claim 49 wherein said multidentate ligand has a bridging atom selected from N and P.

51. The light emitting device of claim 49 wherein said multidentate ligand has a mesityl bridge moiety.

52. The light emitting device of claim 49 wherein said multidentate ligand comprises up to three mono-, bi- or tricyclic heteroaromatic moieties.

53. The light emitting device of claim 1 further comprising an electron blocking layer comprising a compound having the formula:



wherein:

M is a metal atom;

X is N or CX' where X' is H, C₁-C₂₀ alkyl, C₂-C₄₀ mono- or poly alkenyl, C₂-C₄₀ mono- or poly alkynyl, C₃-C₈ cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, or halo;

A is CH, CX', N, P, P(=O), aryl or heteroaryl;

each R¹ and R² is, independently, H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; or

R¹ and R², together with the carbon atoms to which they are attached, link to form a fused C₃-C₈ cycloalkyl or aryl group;

R³ is H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; and

n is 1 to 5.

54. The light emitting device of claim 53 wherein

M is a trivalent metal atom;

X is CH or N;

A is N or 1,3, 5-phenyl;

each R¹ and R² are H, or R¹ and R², together with the carbon atoms to which they are attached, link to form a phenyl group;

R³ is H; and

n is 1 or 2.

55. The light emitting device of claim 53 wherein M is Ga.

56. The light emitting device of claim 53 wherein said electron blocking layer comprises Ga(pma)₃.

57. The light emitting device of claim 53 wherein said metal complex of said hole transporting layer is Co(ppz)₃.

58. The light emitting device of claim 53 wherein said metal complex of said hole transporting layer is FeTp'₂.

59. A light emitting device comprising the substructure HTL/EL or HTL/EBL/EL; wherein each of said EL, HTL, and EBL comprise at least one metal complex.

60. A light emitting device comprising the substructure HTL/EL or HTL/EBL/EL; wherein none of said EL, HTL, or EBL is comprised solely of organic molecules.

61. A light emitting device having a plurality of layers, said device being devoid of a layer that is composed solely of organic molecules.

62. The light emitting device of claim 61 wherein each of said layers contains at least one metal complex.

63. A light emitting device comprising a hole transporting layer, an emissive layer, and a blocking layer;

 said hole transporting layer having a first HOMO energy, wherein said hole transporting layer comprises at least one metal complex;

 said emissive layer comprising at least one material capable of transporting electrons, said material having a second HOMO energy; and

 said blocking layer comprising a material having a HOMO energy that is between said first and second HOMO energies.

64. The device of claim 63 wherein said blocking layer resides between said hole transporting layer and said emissive layer.

65. The device of claim 63 wherein said blocking layer comprises an organic electron blocking material.

66. The light emitting device of claim 65 wherein said organic electron blocking material is selected from triarylaminies or benzidenes.

67. The light emitting device of claim 63 wherein said electron blocking layer comprises a metal complex.

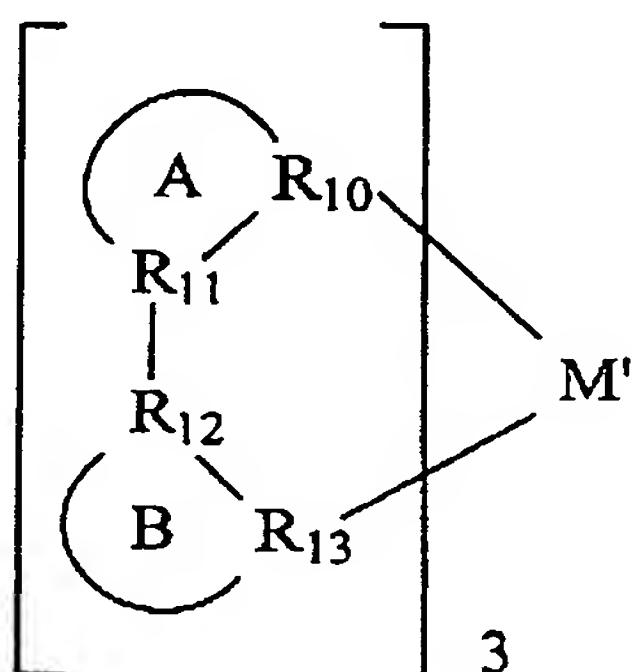
68. A method of facilitating hole transport in a light emitting device, said light emitting device comprising a hole transporting layer and an emissive layer;

said hole transporting layer comprising at least one metal complex and having a first HOMO energy;

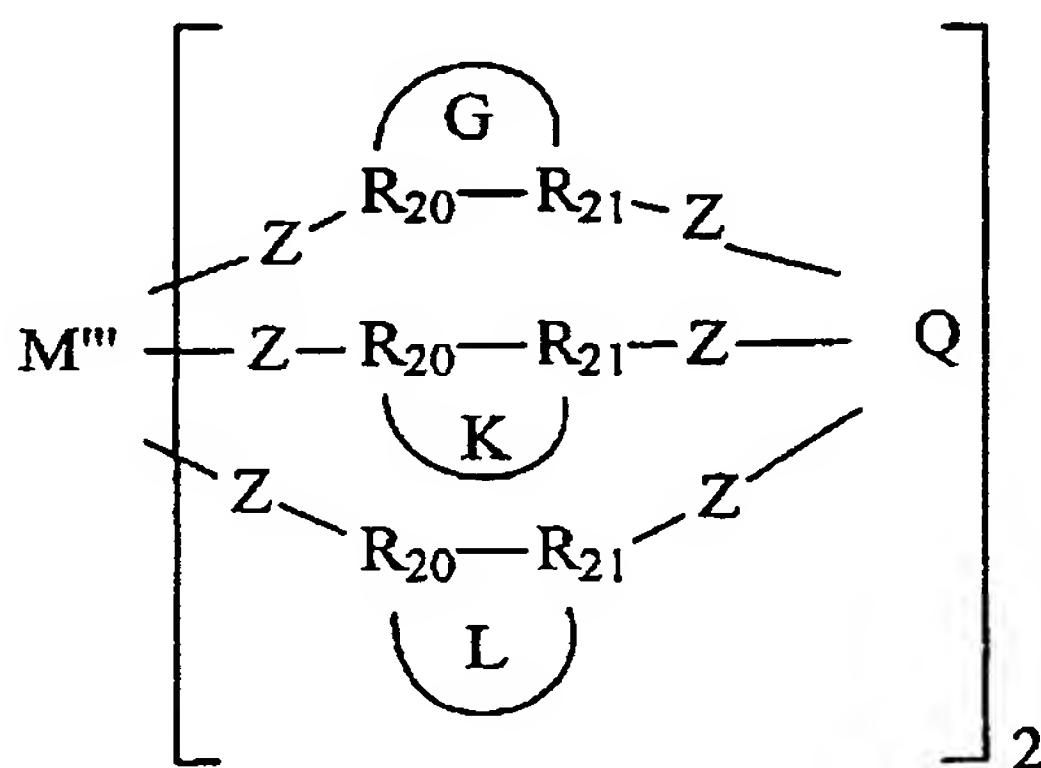
said emissive layer comprising at least one material capable of transporting electrons, said material having a second HOMO energy higher than said HOMO energy of said hole transporting layer;

said method comprising the step of placing a blocking layer between said hole transporting layer and said emissive layer, wherein said blocking layer comprises a material having a HOMO energy level that is between said first and second HOMO energies.

69. The method of claim 68 wherein said metal complex of said hole transporting layer is a complex formula I or II:



I



II

wherein:

M' and M''' are each, independently, a metal atom;

R_{10} , R_{13} , R_{20} and R_{21} are each, independently, N or CH;

R_{11} and R_{12} are each, independently, N, CH, O or S;

Ring systems A, B, G, K and L are each independently a mono-, di- or tricyclic fused aliphatic or aromatic ring system optionally containing up to 5 hetero atoms;

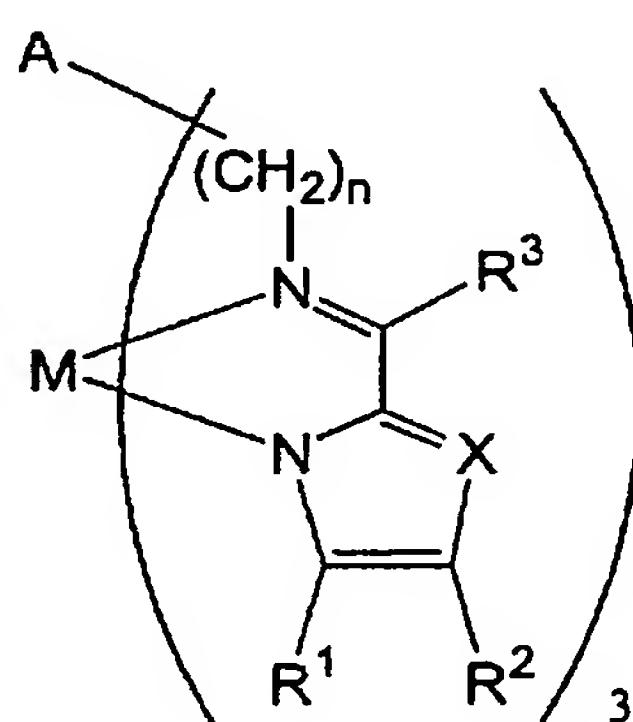
Z is C₁-C₆ alkyl, C₂-C₈ mono- or poly alkenyl, C₂-C₈ mono- or poly alkynyl, or a bond; and

Q is BH, N, or CH.

70. The method of claim 68 wherein said metal complex of said hole transporting layer is Co(ppz)₃ or FeTp'₂.

71. The method of claim 68 wherein said blocking layer comprises at least one metal complex.

72. The method of claim 71 wherein said metal complex of said blocking layer is a compound having the formula:



wherein:

M is a metal atom;

X is N or CX' where X' is H, C₁-C₂₀ alkyl, C₂-C₄₀ mono- or poly alkenyl, C₂-C₄₀ mono- or poly alkynyl, C₃-C₈ cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, or halo;

A is CH, CX', N, P, P(=O), aryl or heteroaryl;

each R¹ and R² is, independently, H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; or

R¹ and R², together with the carbon atoms to which they are attached, link to form a fused C₃-C₈ cycloalkyl or aryl group;

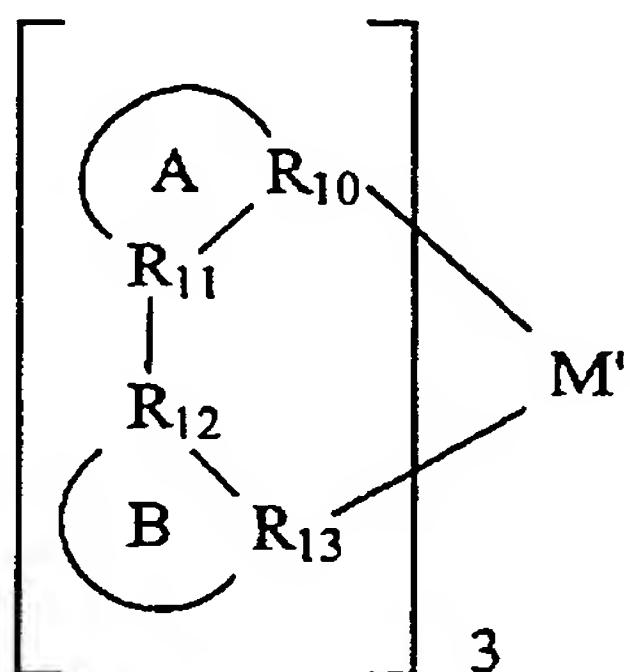
R³ is H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; and

n is 1 to 5.

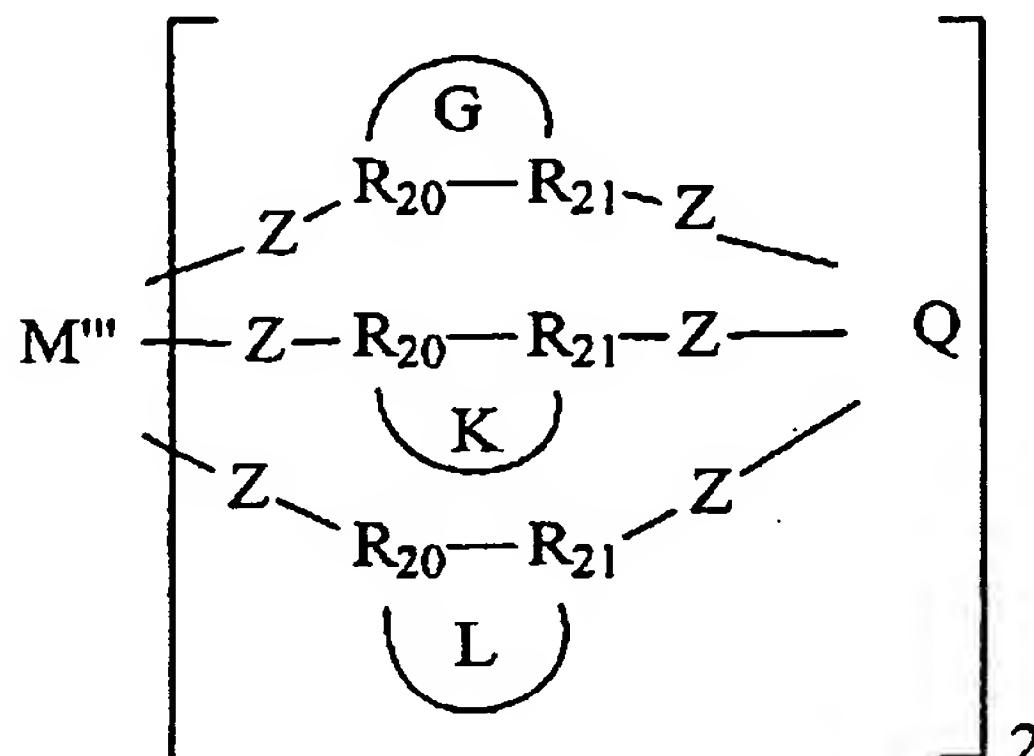
73. The method of claim 71 wherein said metal complex of said blocking layer is Ga(pma)₃.

74. The method of claim 68 wherein said hole transporting layer comprises Co(ppz)₃ or FeTp'₂, and said barrier layer comprises Ga(pma)₃.

75. A method of fabricating a light emitting device, said method comprising placing a hole transporting layer in electrical contact with an emissive layer, wherein said hole transporting layer comprises a compound of formulas I or II:



I



II

wherein:

M' and M''' are each, independently, a metal atom;

R₁₀, R₁₃, R₂₀ and R₂₁ are each, independently, N or CH;

R₁₁ and R₁₂ are each, independently, N, CH, O or S;

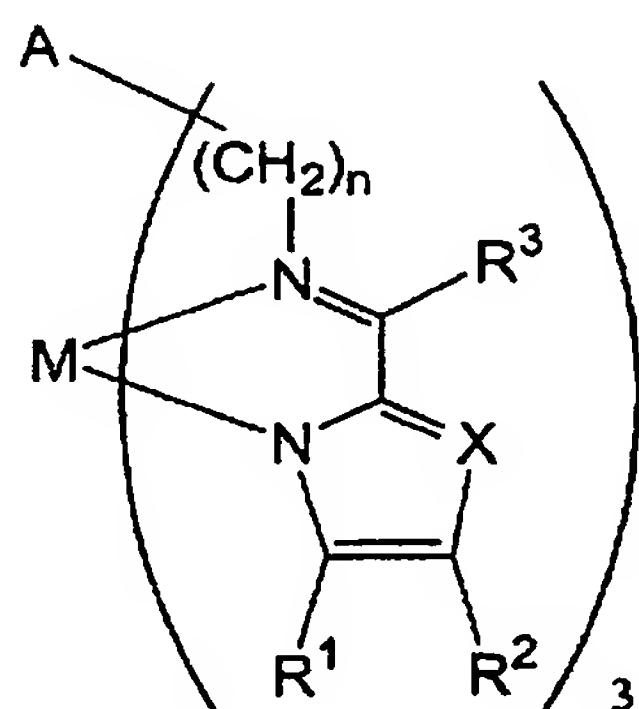
Ring systems A, B, G, K and L are each independently a mono-, di- or tricyclic fused aliphatic or aromatic ring system optionally containing up to 5 hetero atoms;

Z is C₁-C₆ alkyl, C₂-C₈ mono- or poly alkenyl, C₂-C₈ mono- or poly alkynyl, or a bond; and

Q is BH, N, or CH.

76. The method of claim 75 wherein said light emitting device further comprises an electron blocking layer.

77. The method of claim 76 wherein said electron blocking layer comprises a compound having the formula:



wherein:

M is a metal atom;

X is N or CX' where X' is H, C₁-C₂₀ alkyl, C₂-C₄₀ mono- or poly alkenyl, C₂-C₄₀ mono- or poly alkynyl, C₃-C₈ cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, or halo;

A is CH, CX', N, P, P(=O), aryl or heteroaryl;

each R¹ and R² is, independently, H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; or

R¹ and R², together with the carbon atoms to which they are attached, link to form a fused C₃-C₈ cycloalkyl or aryl group;

R³ is H, C₁-C₂₀ alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₃-C₈ cycloalkyl, aryl, aralkyl, or halo; and

n is 1 to 5.

78. The method of claim 76 wherein said electron blocking layer comprises Ga(pma)₃.

79. The method of claim 75 wherein said compound is Co(ppz)₃ or FeTp'₂.

80. The method of claim 75 wherein said compound is Co(ppz)₃.

81. A method of transporting holes in a hole transporting layer of a light emitting device, wherein said hole transporting layer comprises at least one metal complex, said method comprising applying a voltage across said device.

82. A pixel comprising the light emitting device of claim 1.

83. A pixel comprising the light emitting device of claim 14.

84. A pixel comprising the light emitting device of claim 27.

85. A pixel comprising the light emitting device of claim 38.

86. A pixel comprising the light emitting device of claim 53.

87. A pixel comprising the light emitting device of claim 63.

88. An electronic display comprising the light emitting device of claim 1.

89. An electronic display comprising the light emitting device of claim 14.

90. An electronic display comprising the light emitting device of claim 27.

91. An electronic display comprising the light emitting device of claim 38.

92. An electronic display comprising the light emitting device of claim 53.

93. An electronic display comprising the light emitting device of claim 63.

FIGURE 1

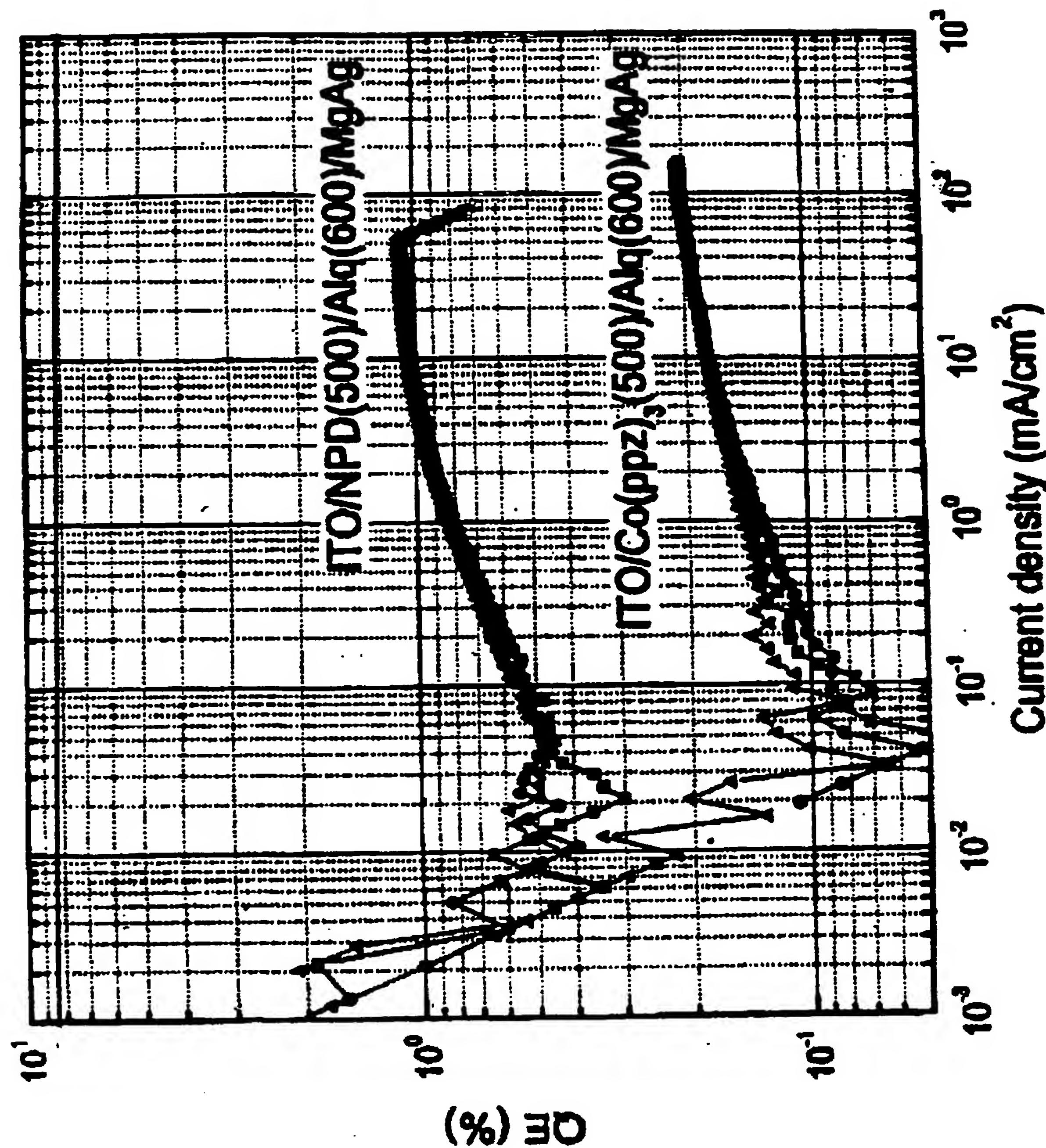


FIGURE 2

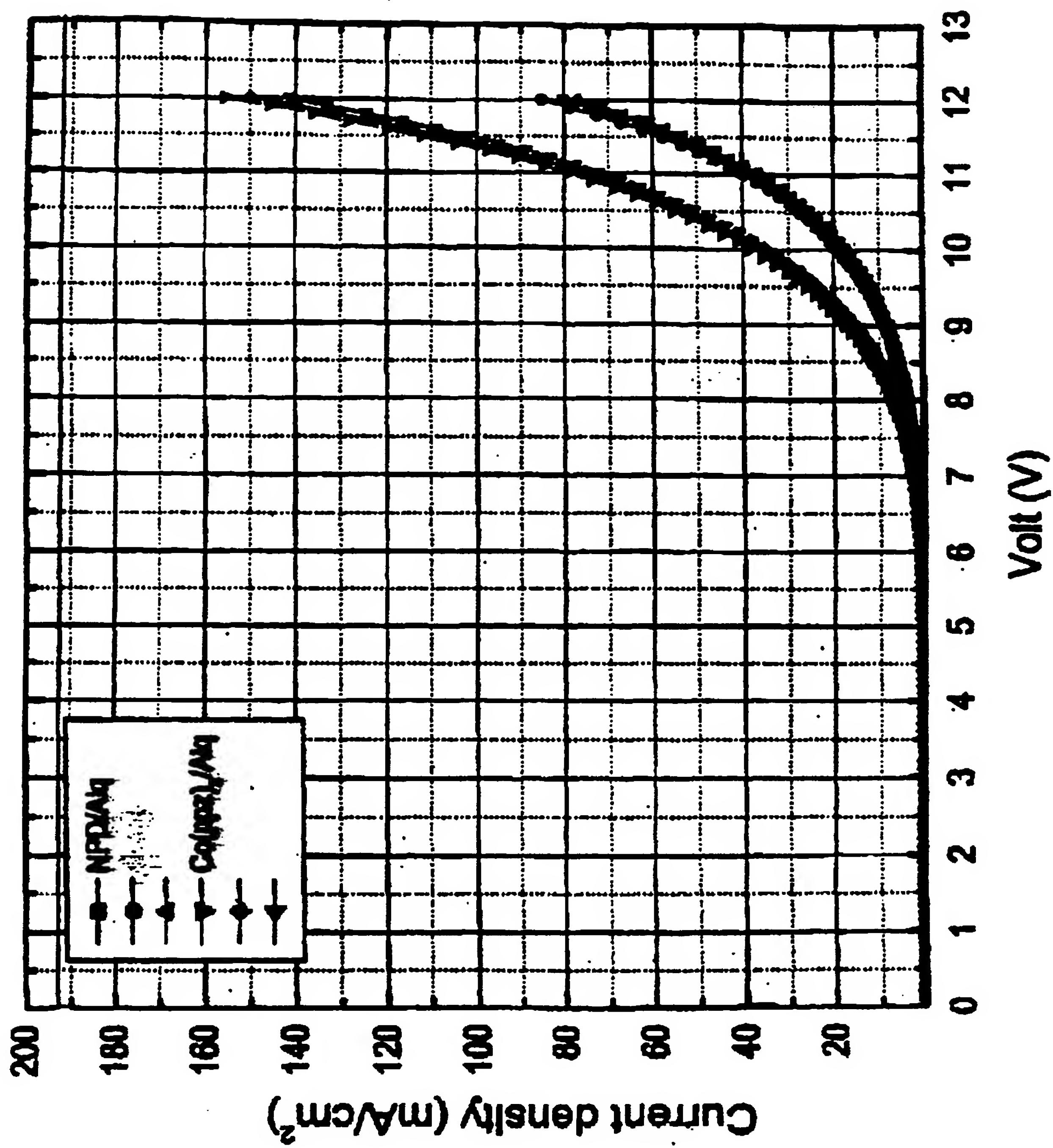


FIGURE 3

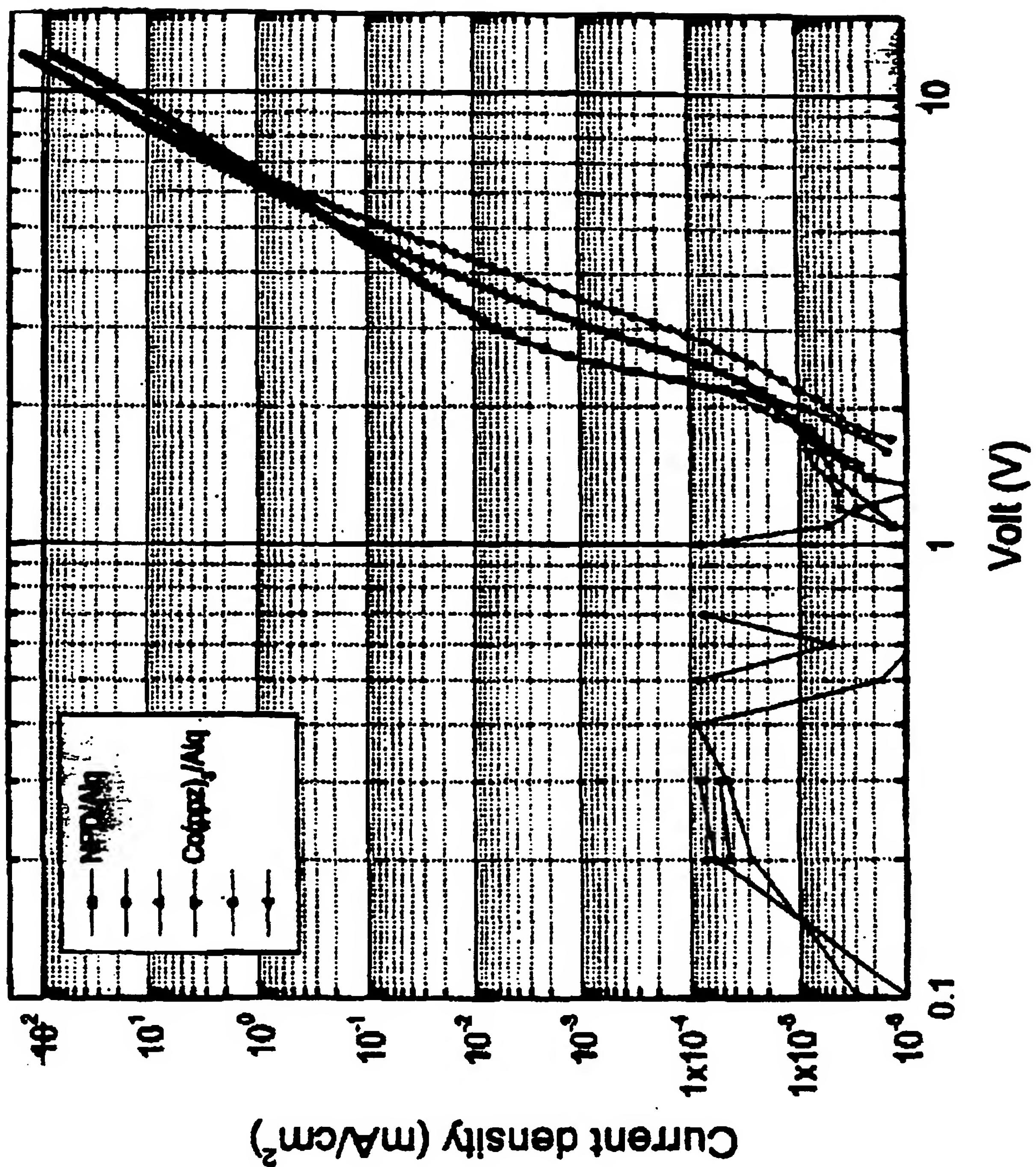


FIGURE 4A

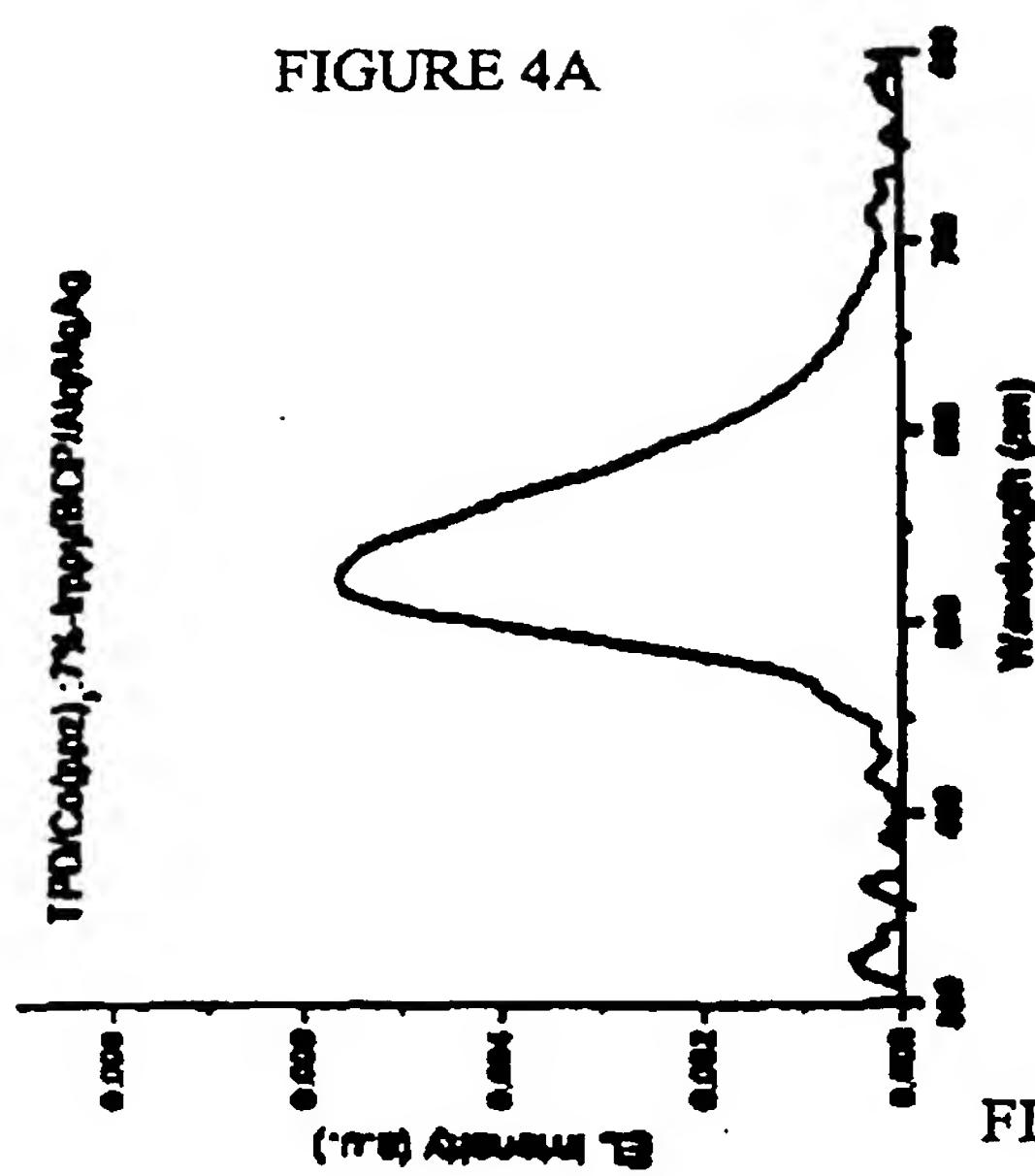


FIGURE 4B

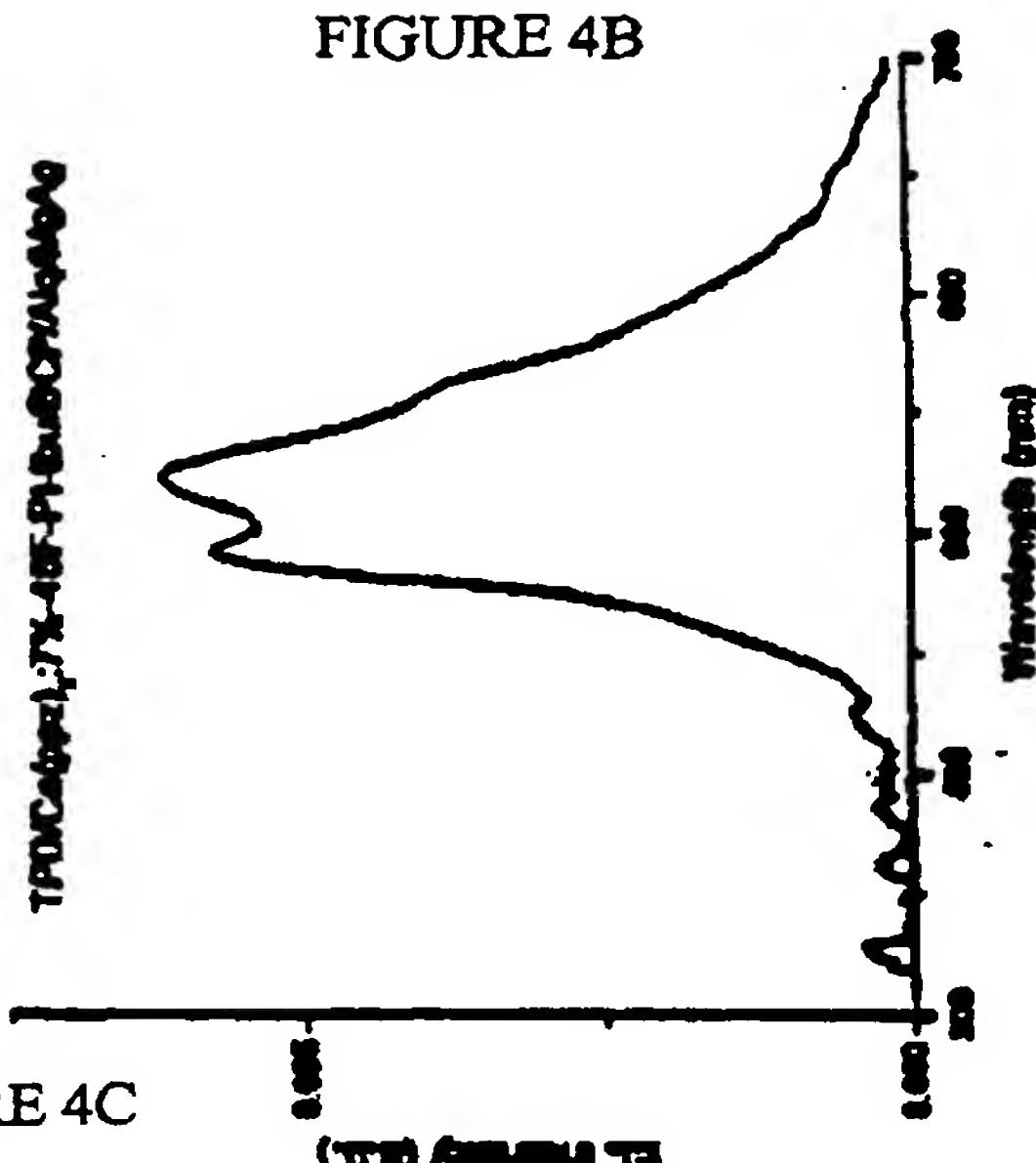


FIGURE 4C

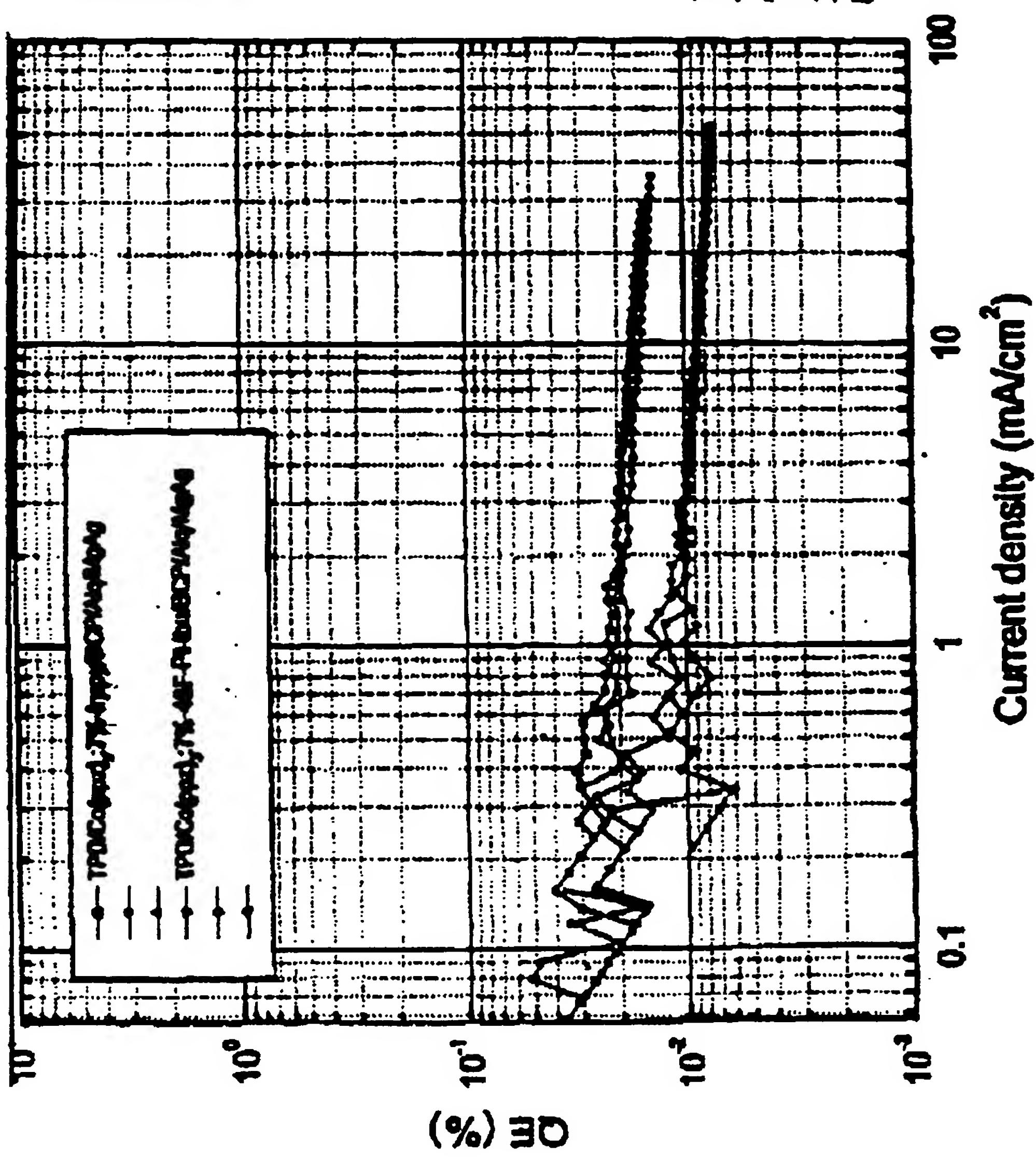


FIGURE 5

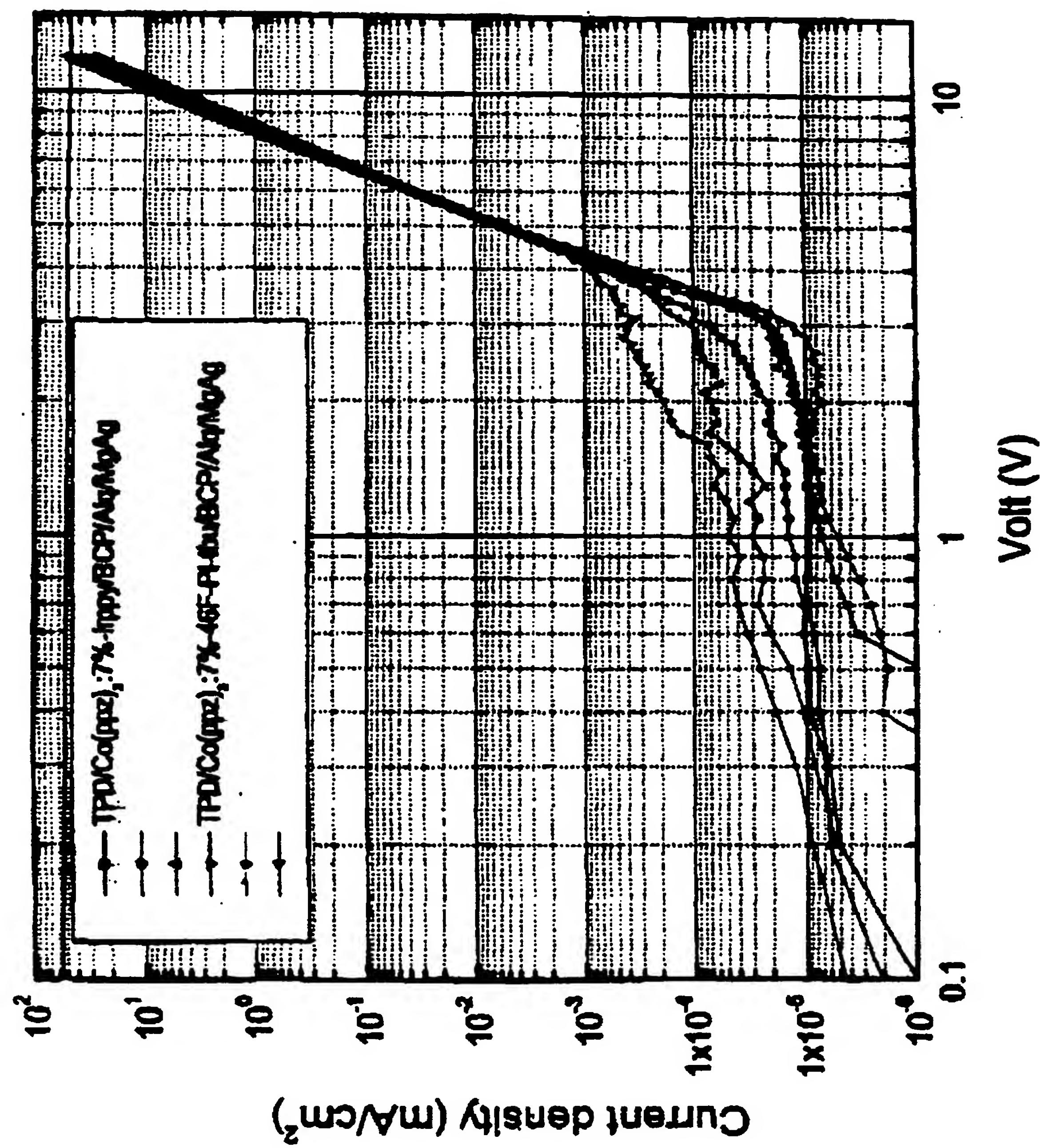


FIGURE 6A

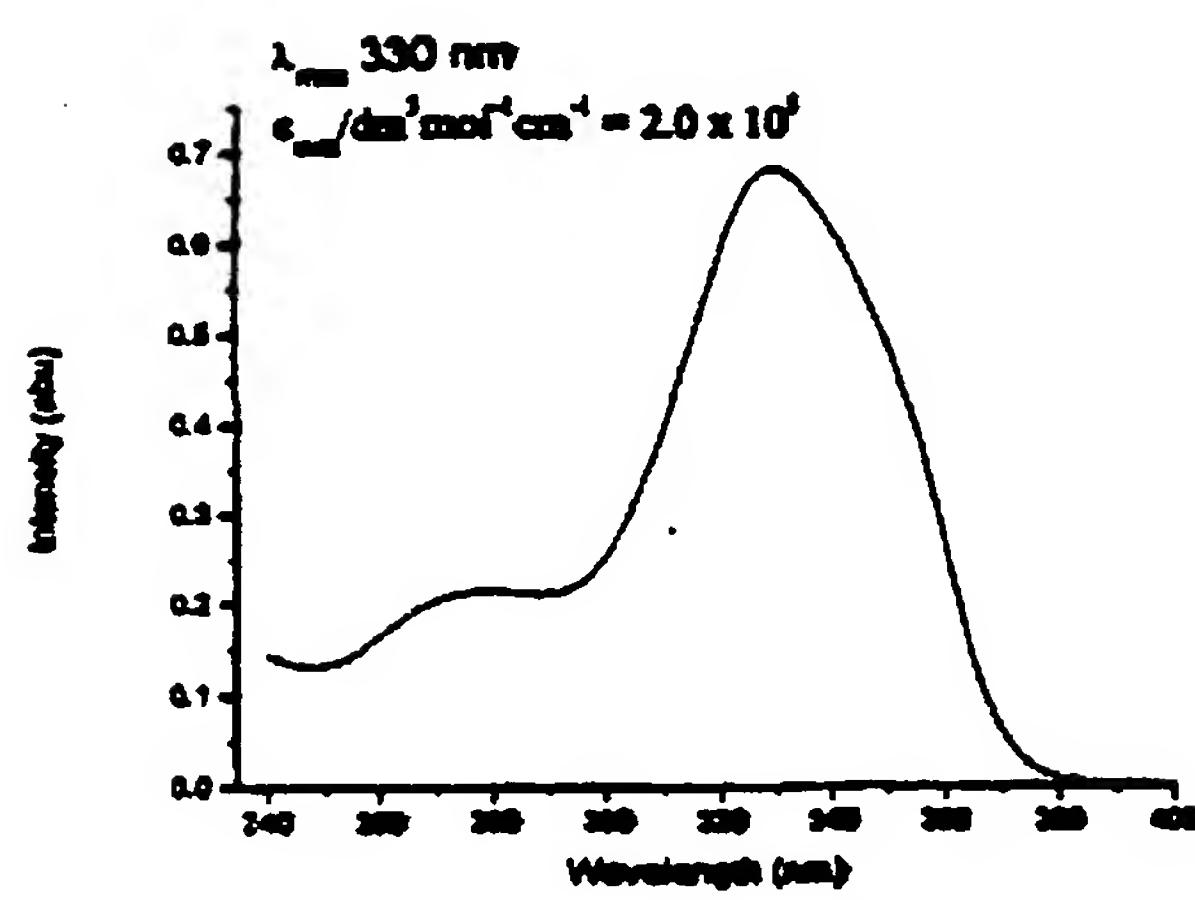


FIGURE 6B

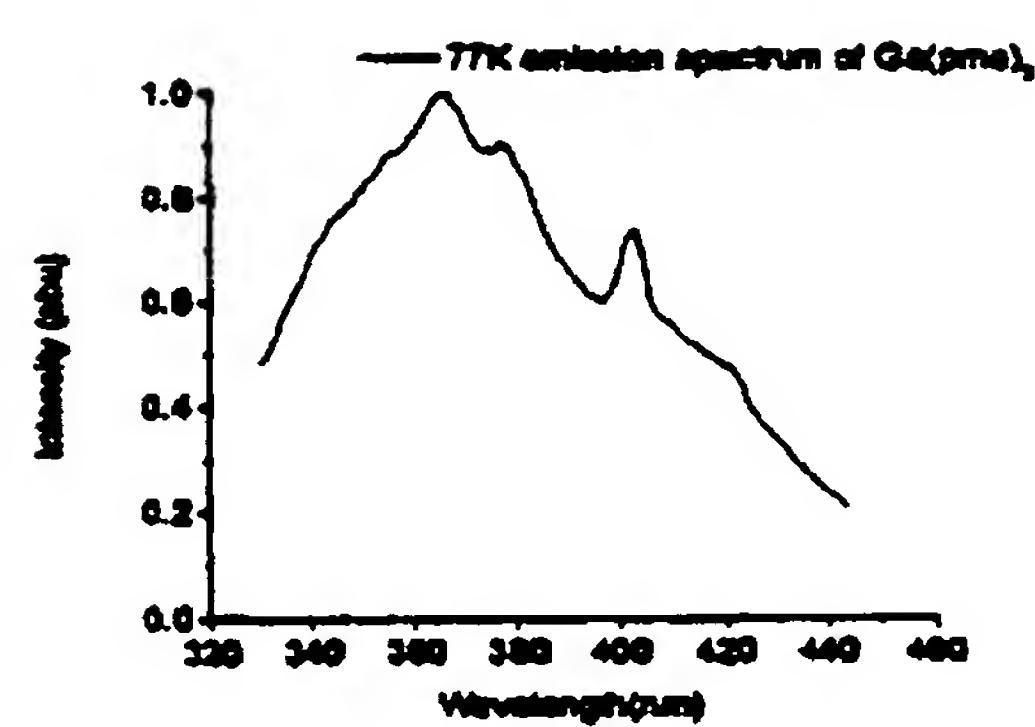


FIGURE 7

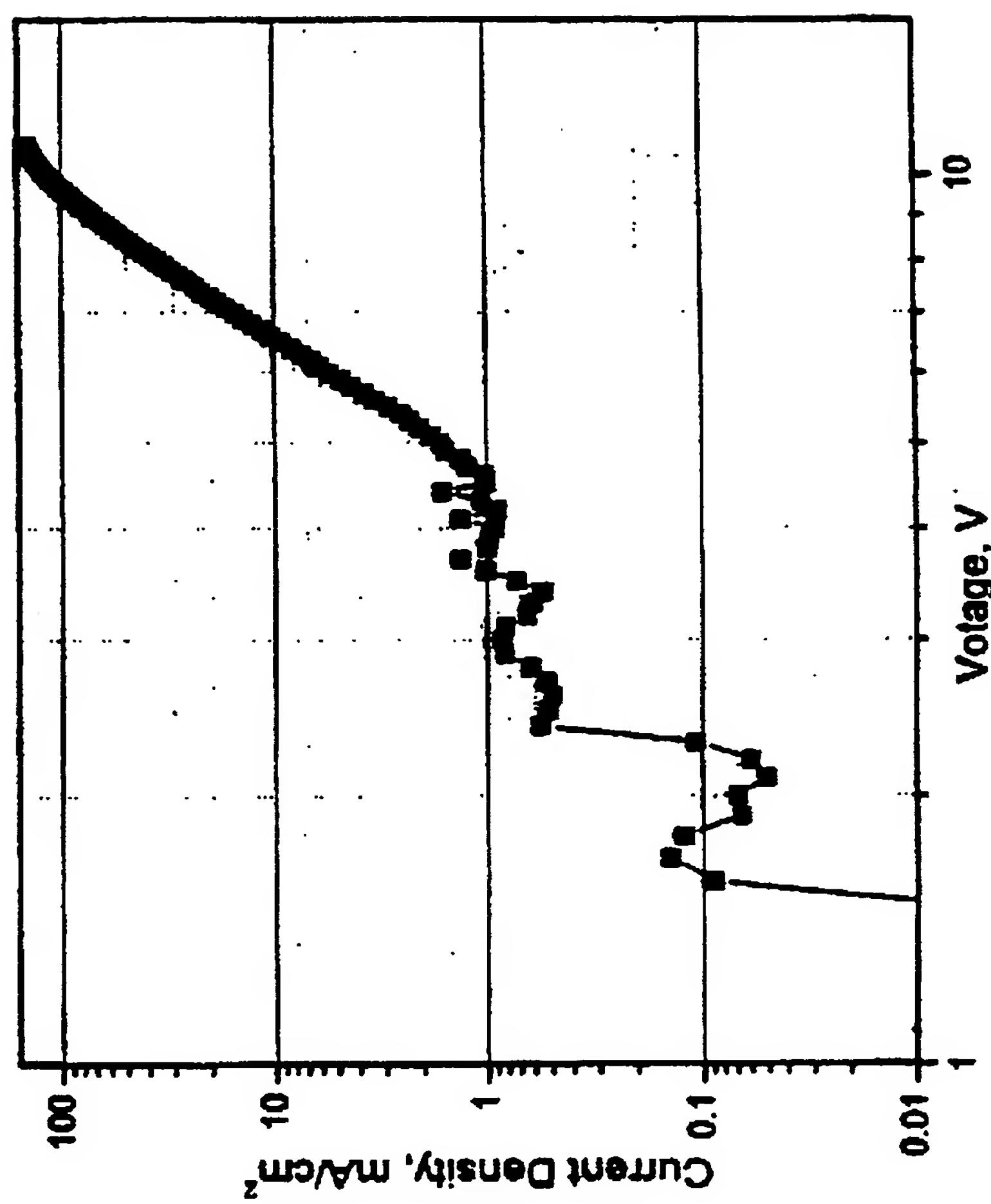
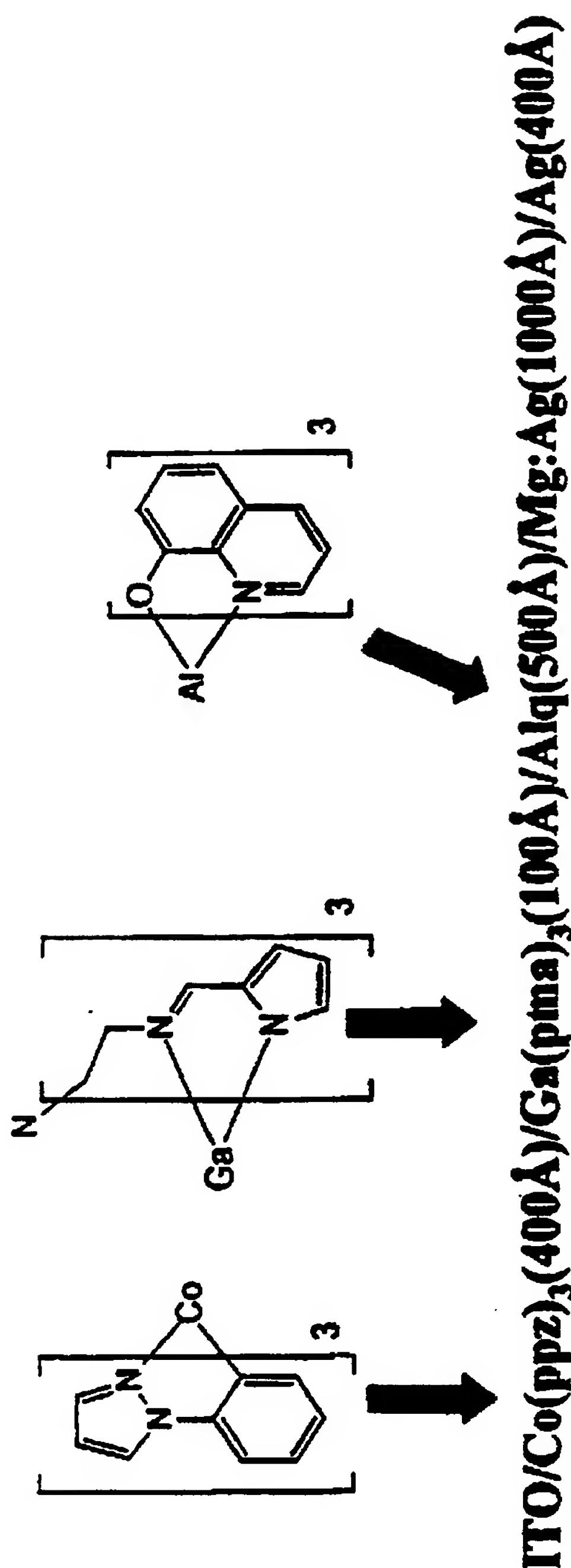


FIGURE 8

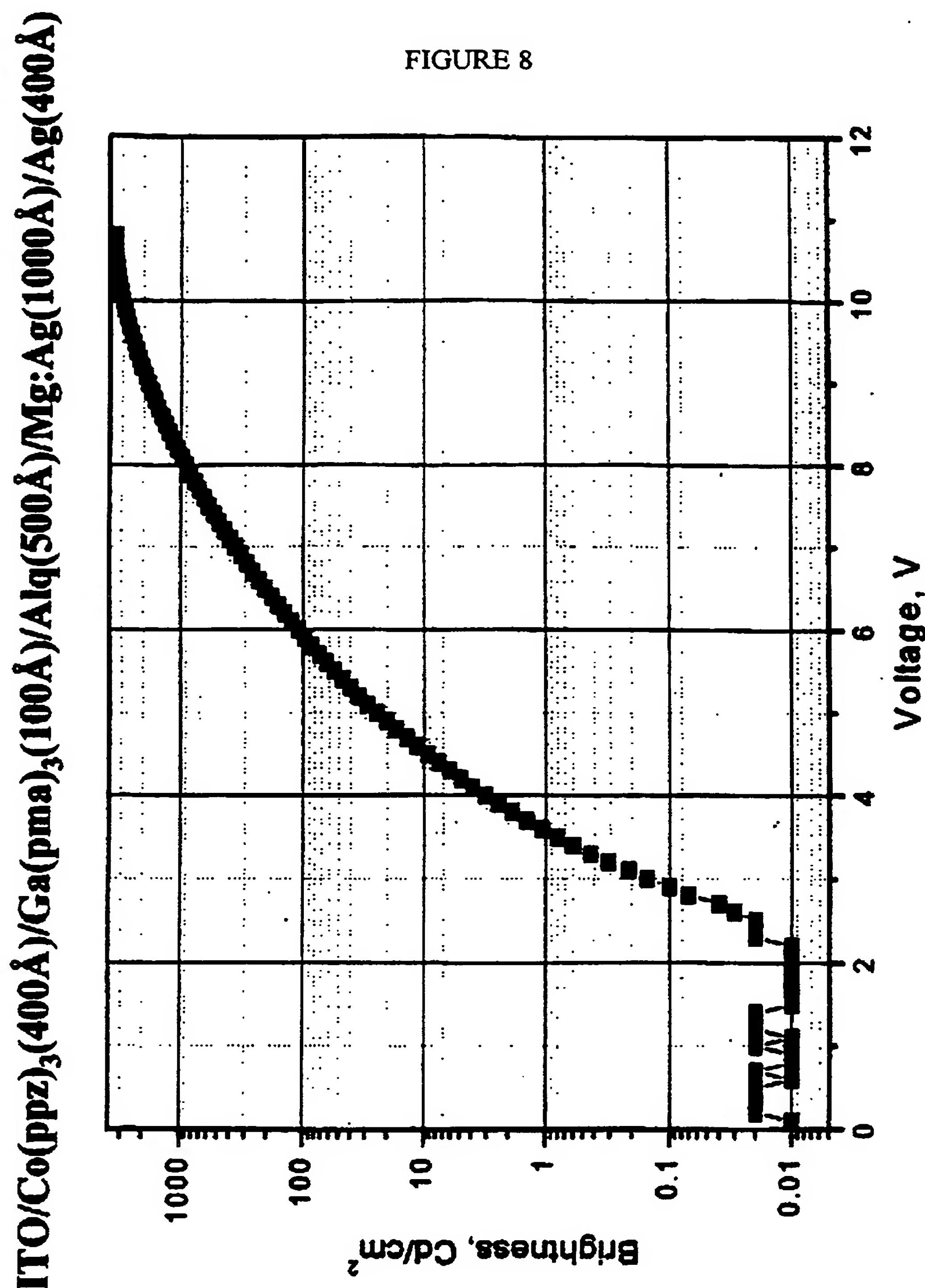


FIGURE 9

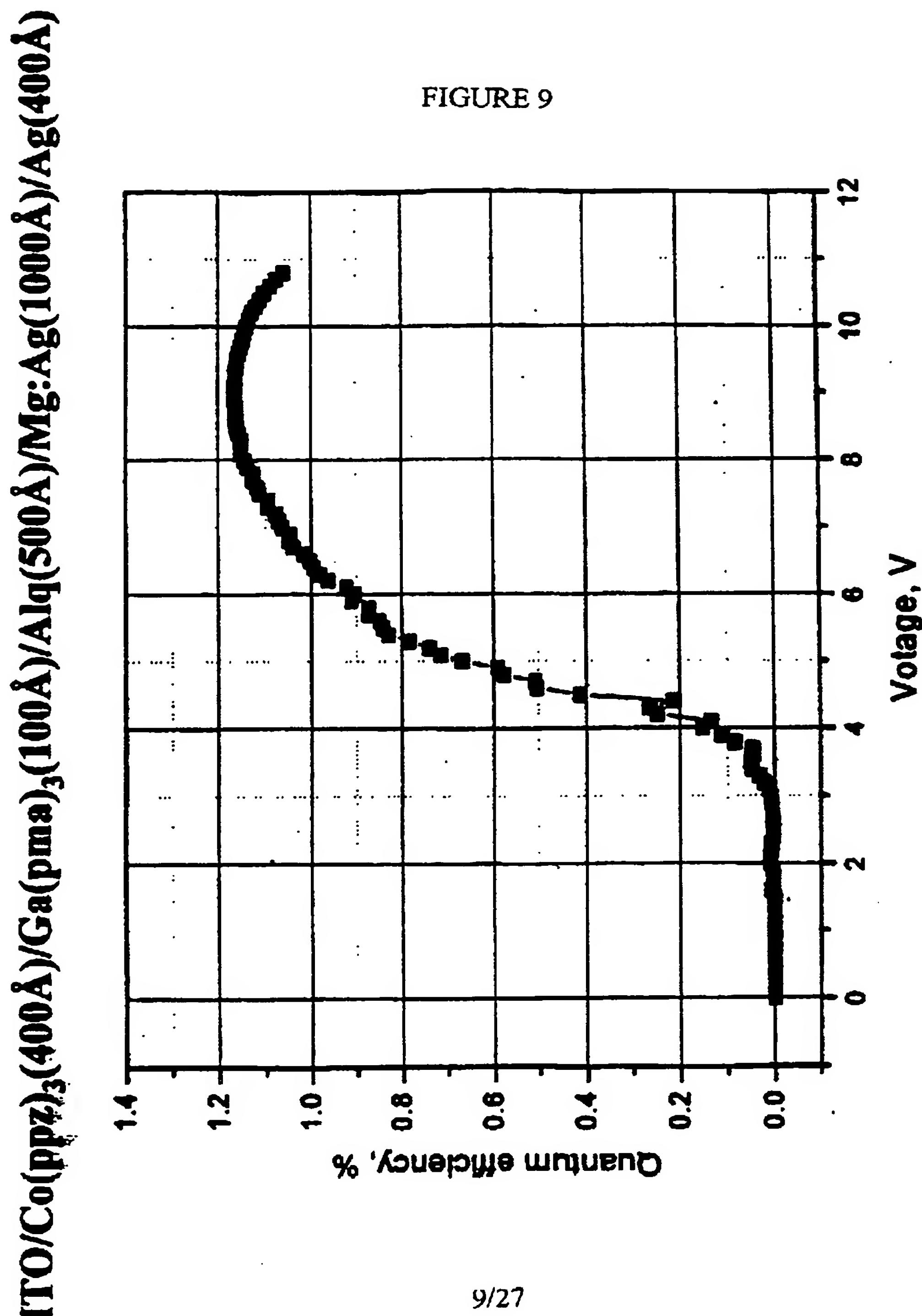
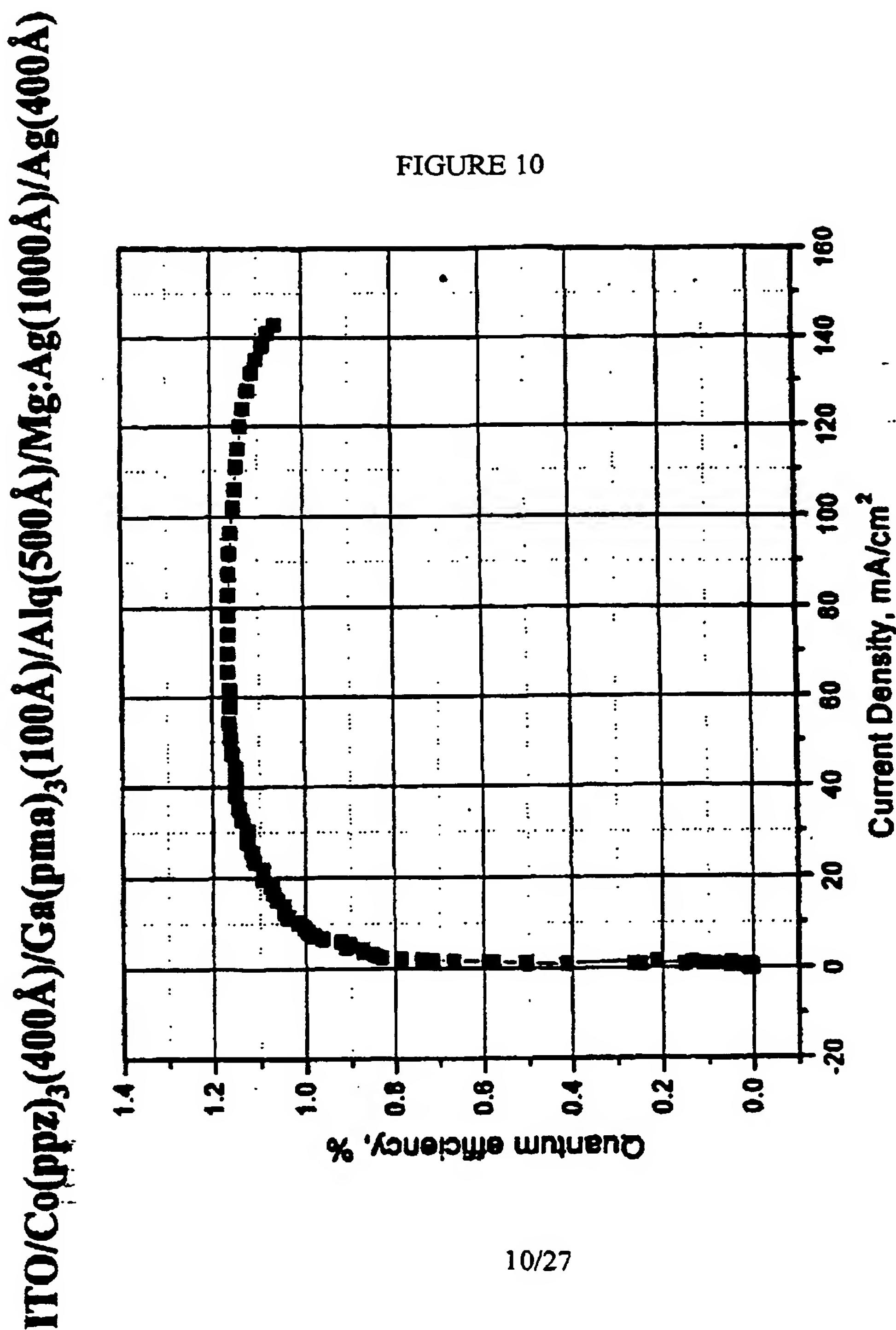
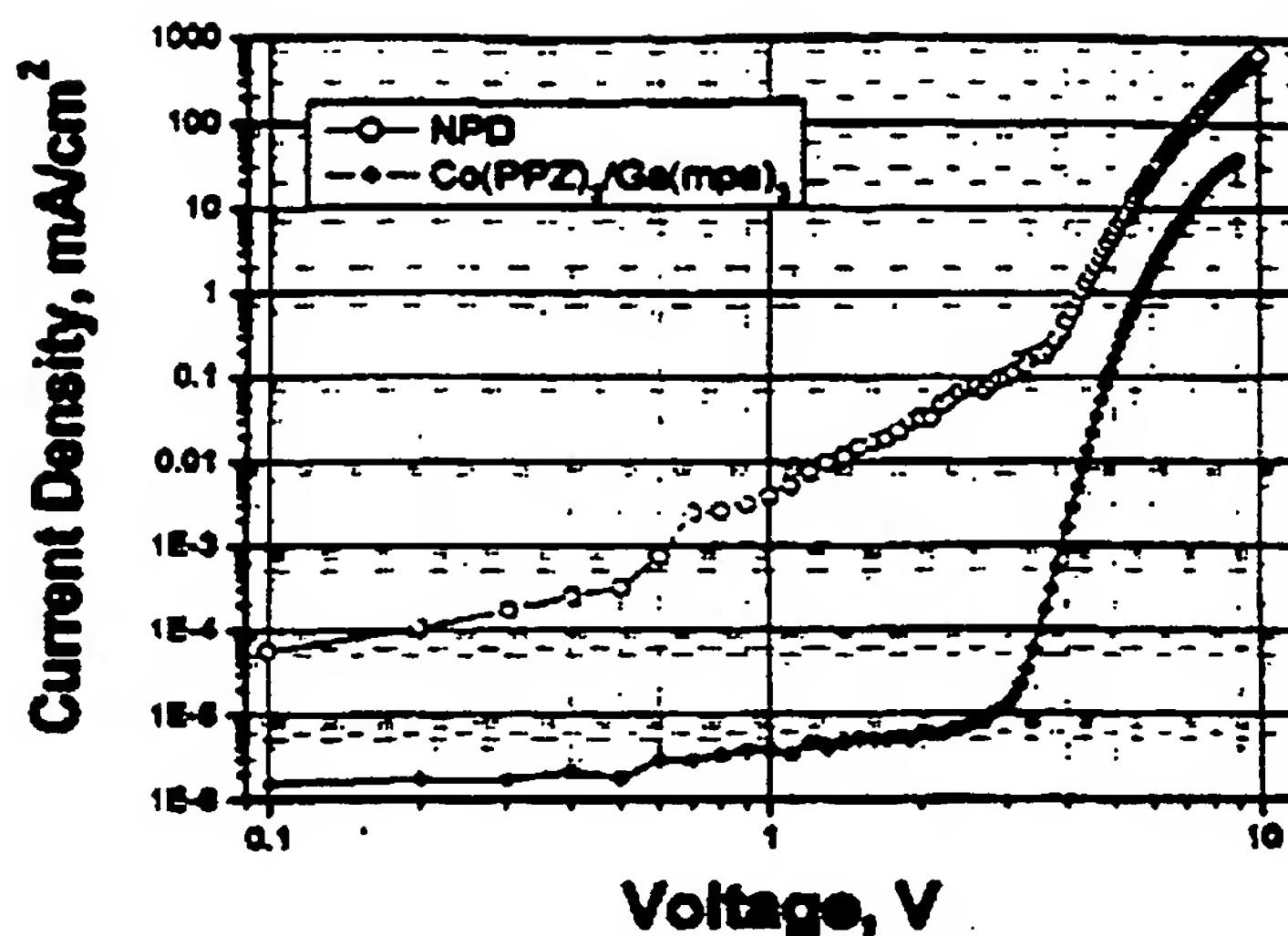


FIGURE 10



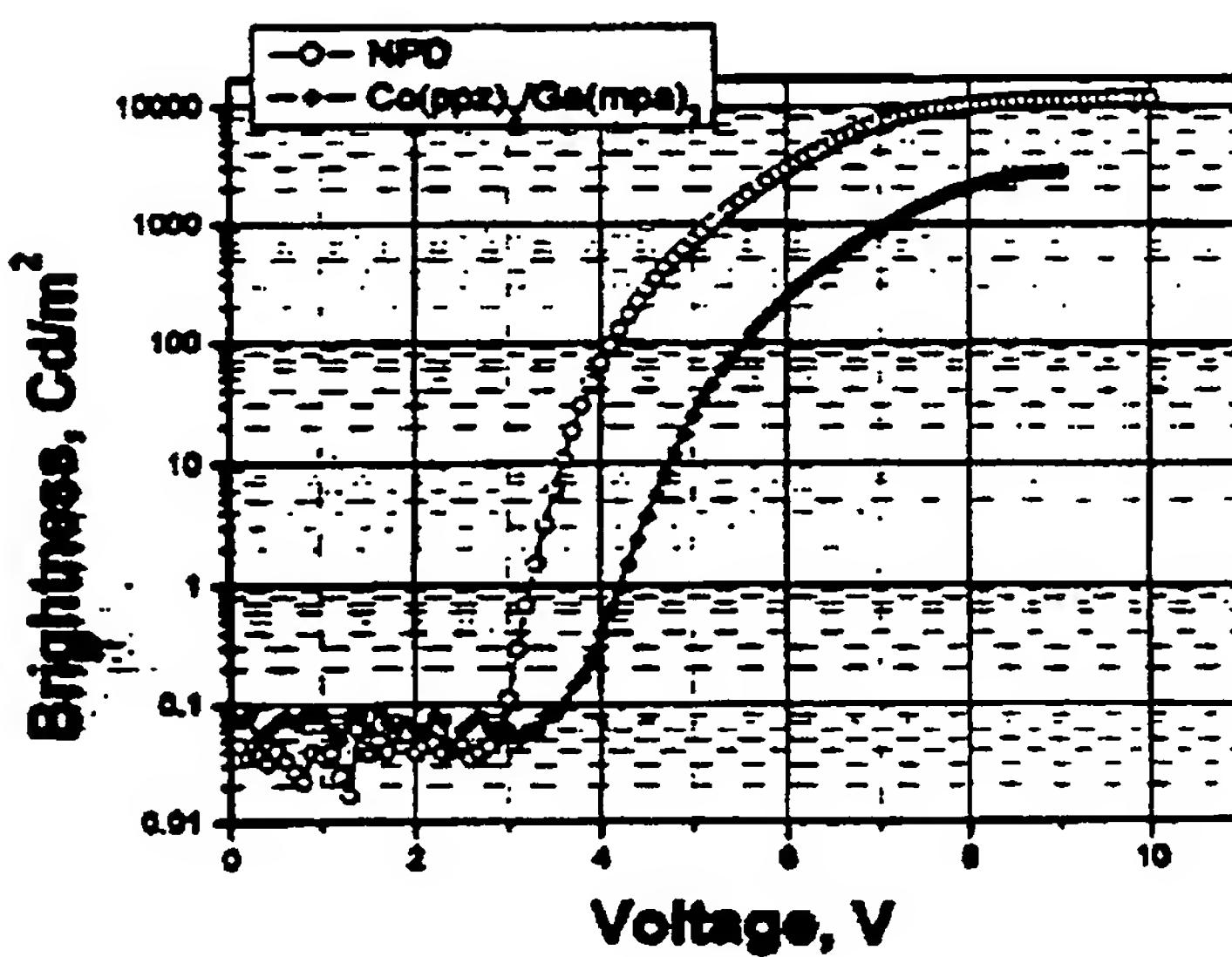
10/27

FIGURE 11A



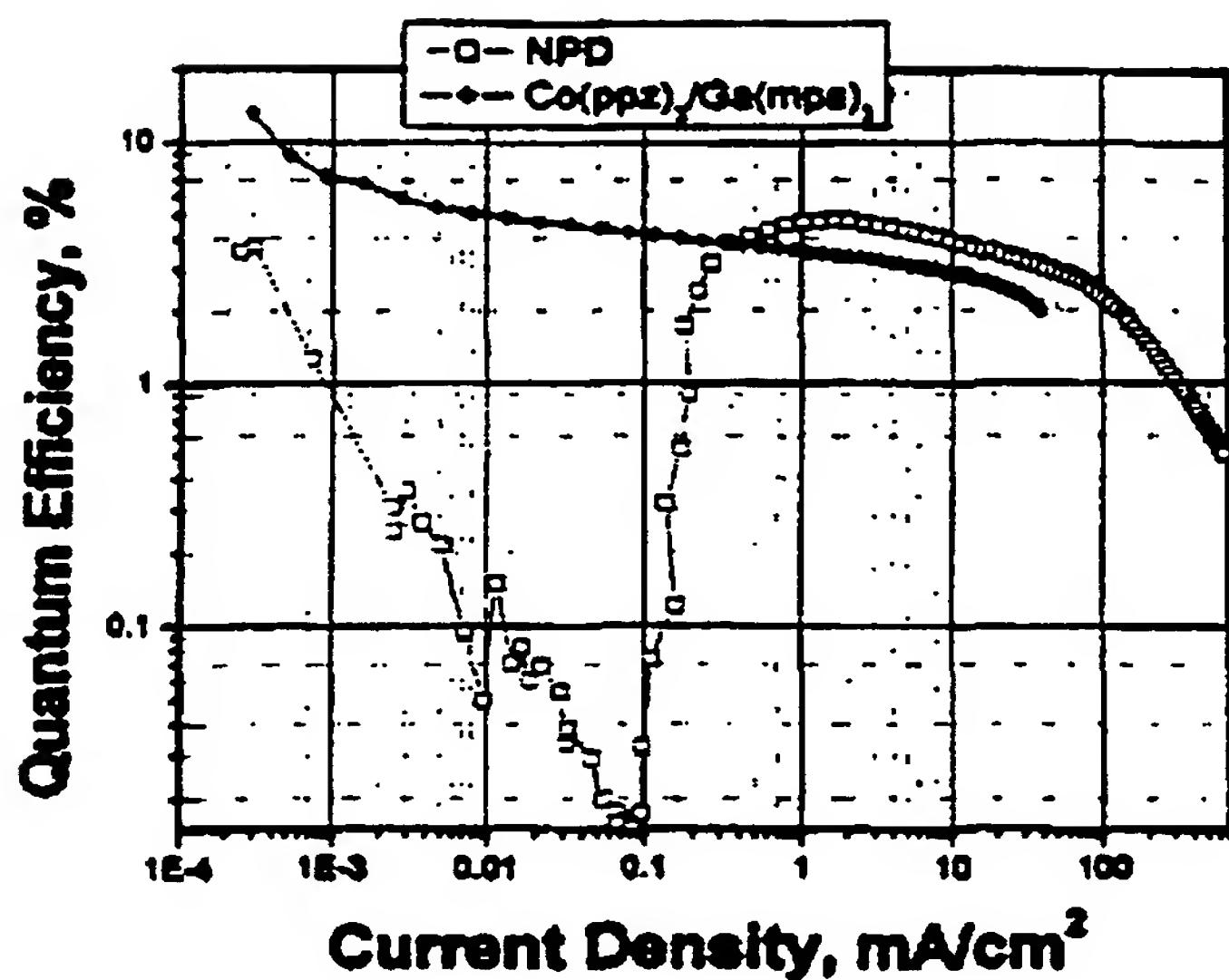
I-V characteristics for NPD and Co(ppz)₃/Ga(mpa)₃ based OLEDs. Device structure: ITO/HTL(300Å)/CBP:Irppy(6% 200Å)/BCP(150Å)/Alq₃(200Å)/LiF/Al

FIGURE 11B



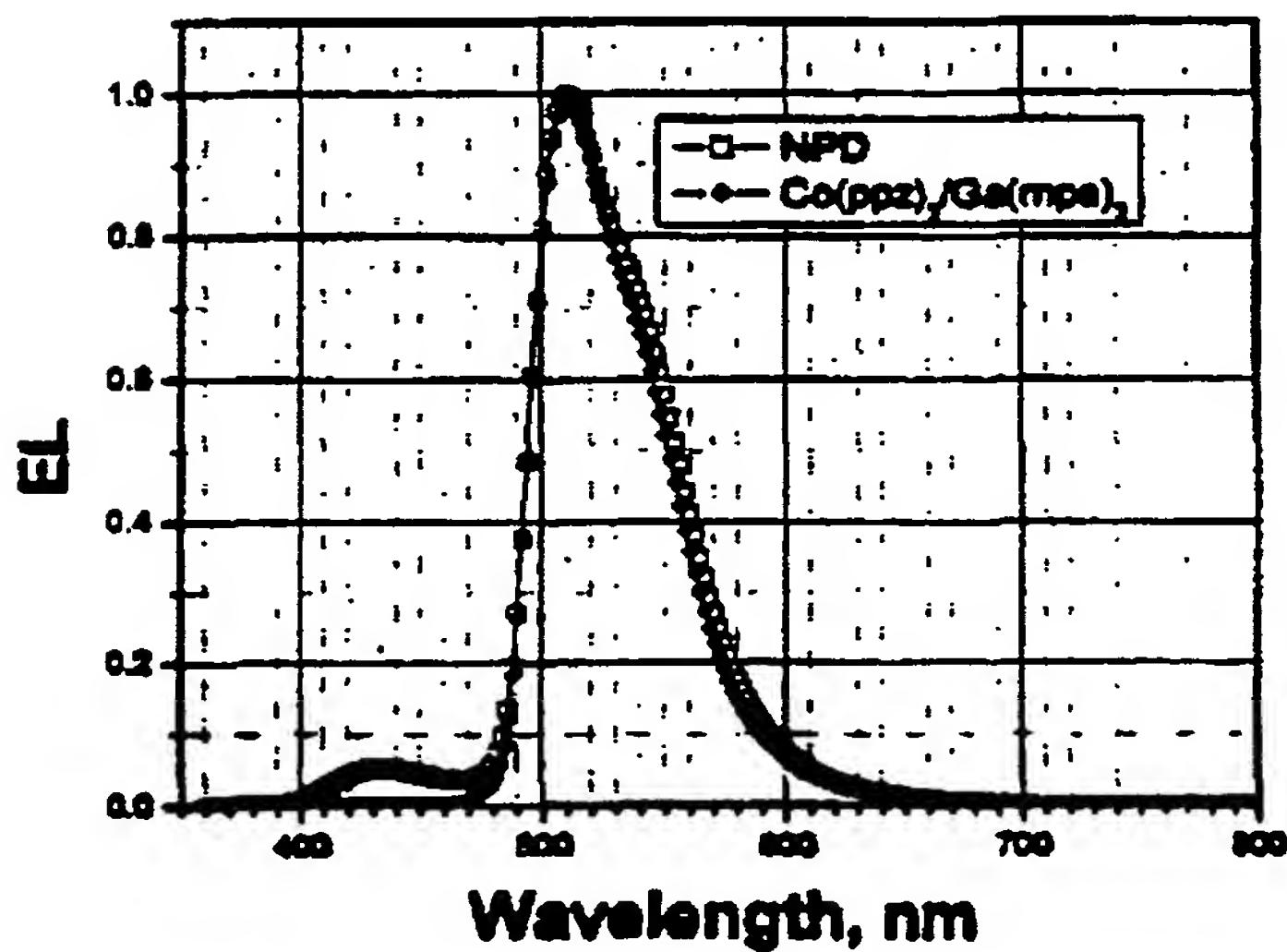
Brightness versus voltage for devices of Figure 7.

FIGURE 12A



Quantum efficiency versus current density for the devices of Figure 7.

FIGURE 12B



Emission spectra for the devices of Figure 7.

FIGURE 13

ITO/CuPPIZ(400Å)/NPD(100Å)/Al_x(500Å)/Mg₂Ag(1000Å)/Ag(400Å)

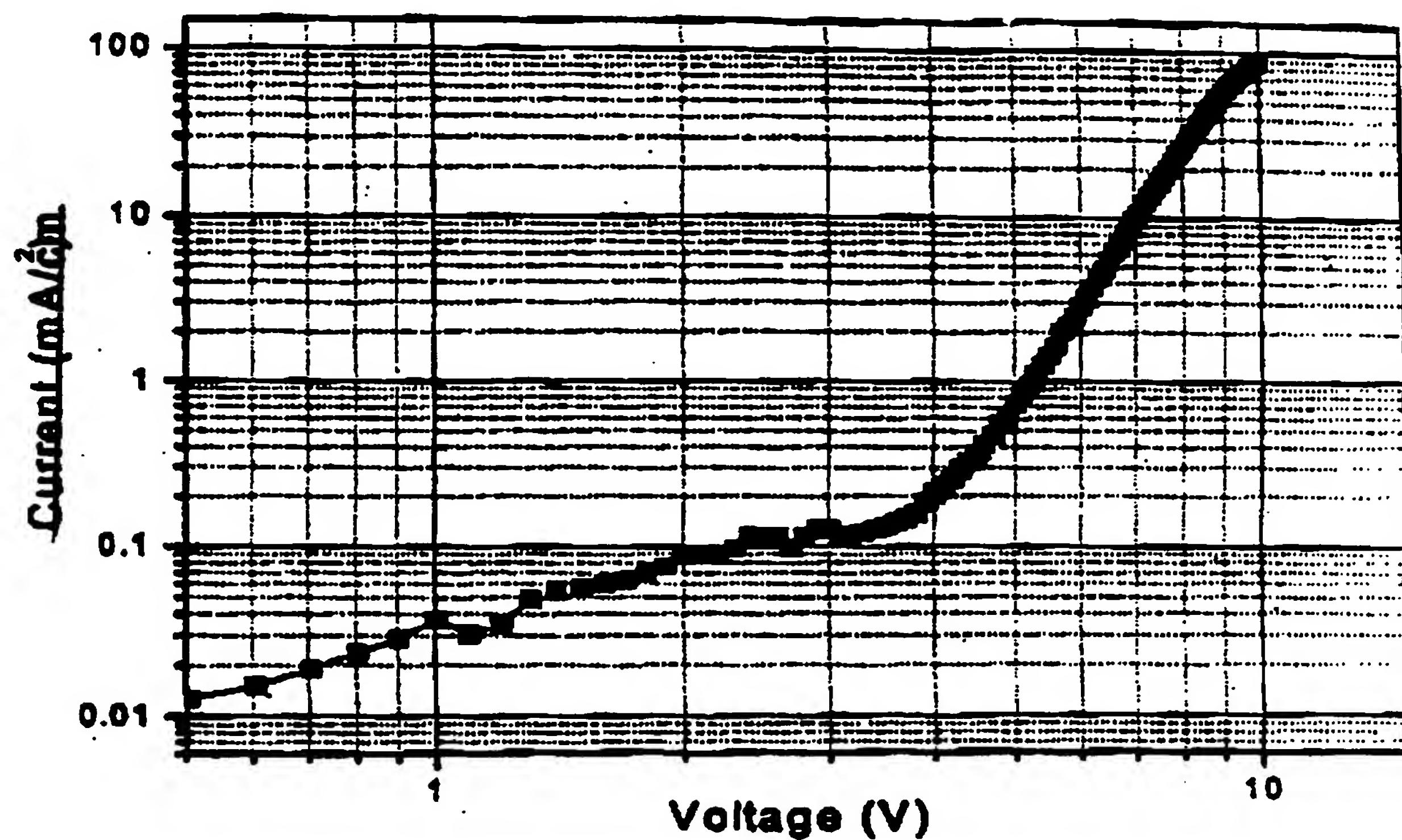


FIGURE 14

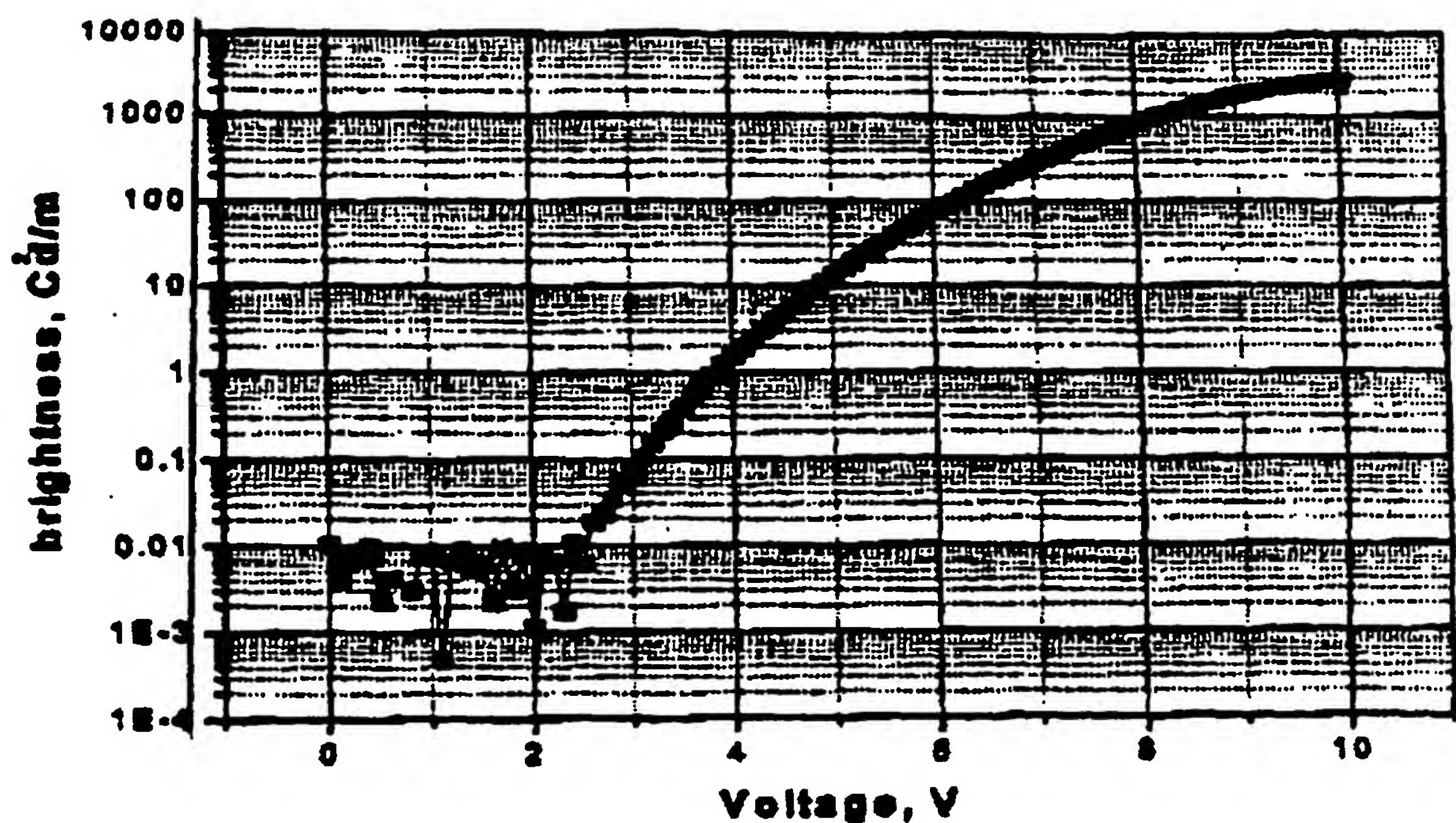
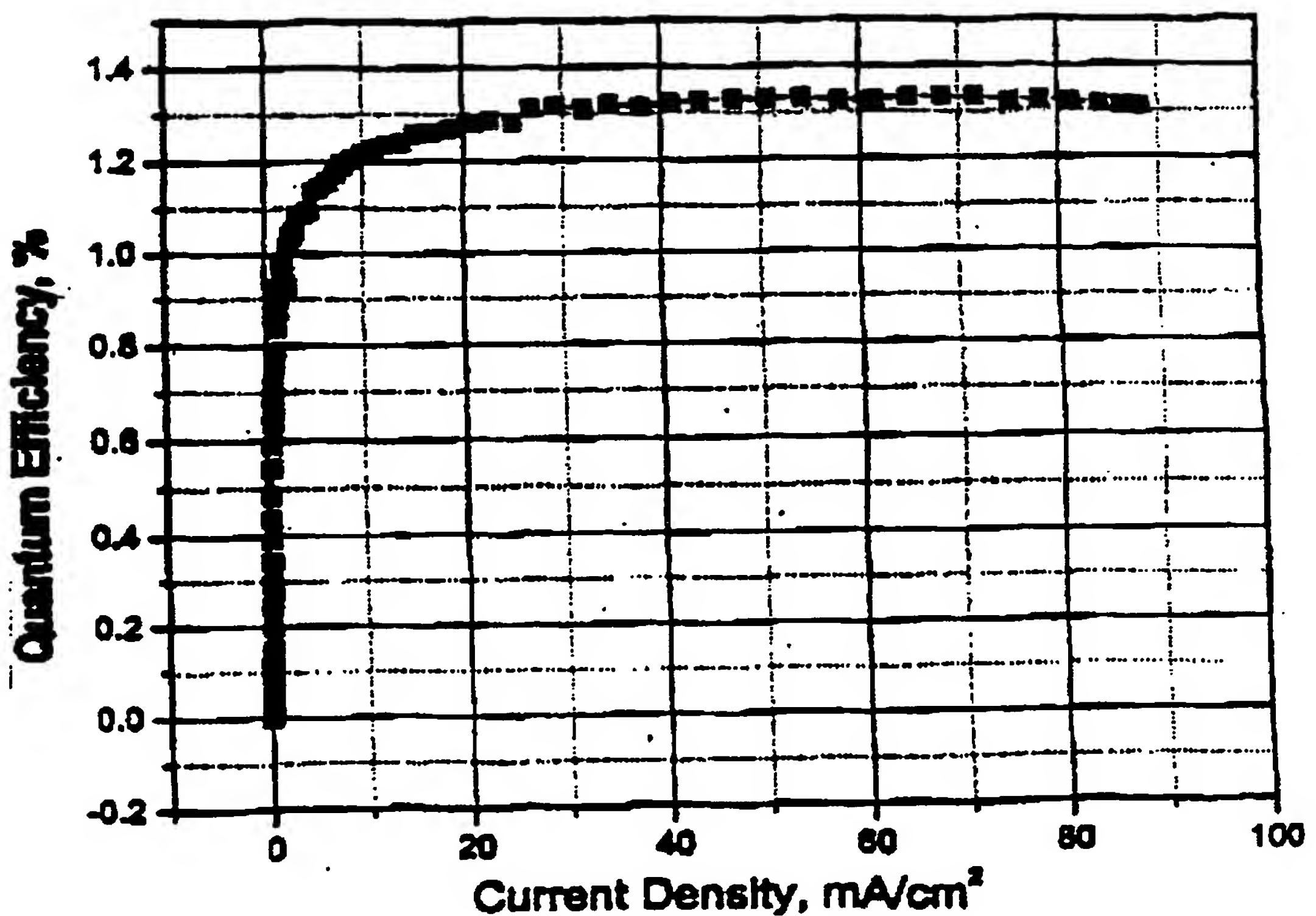
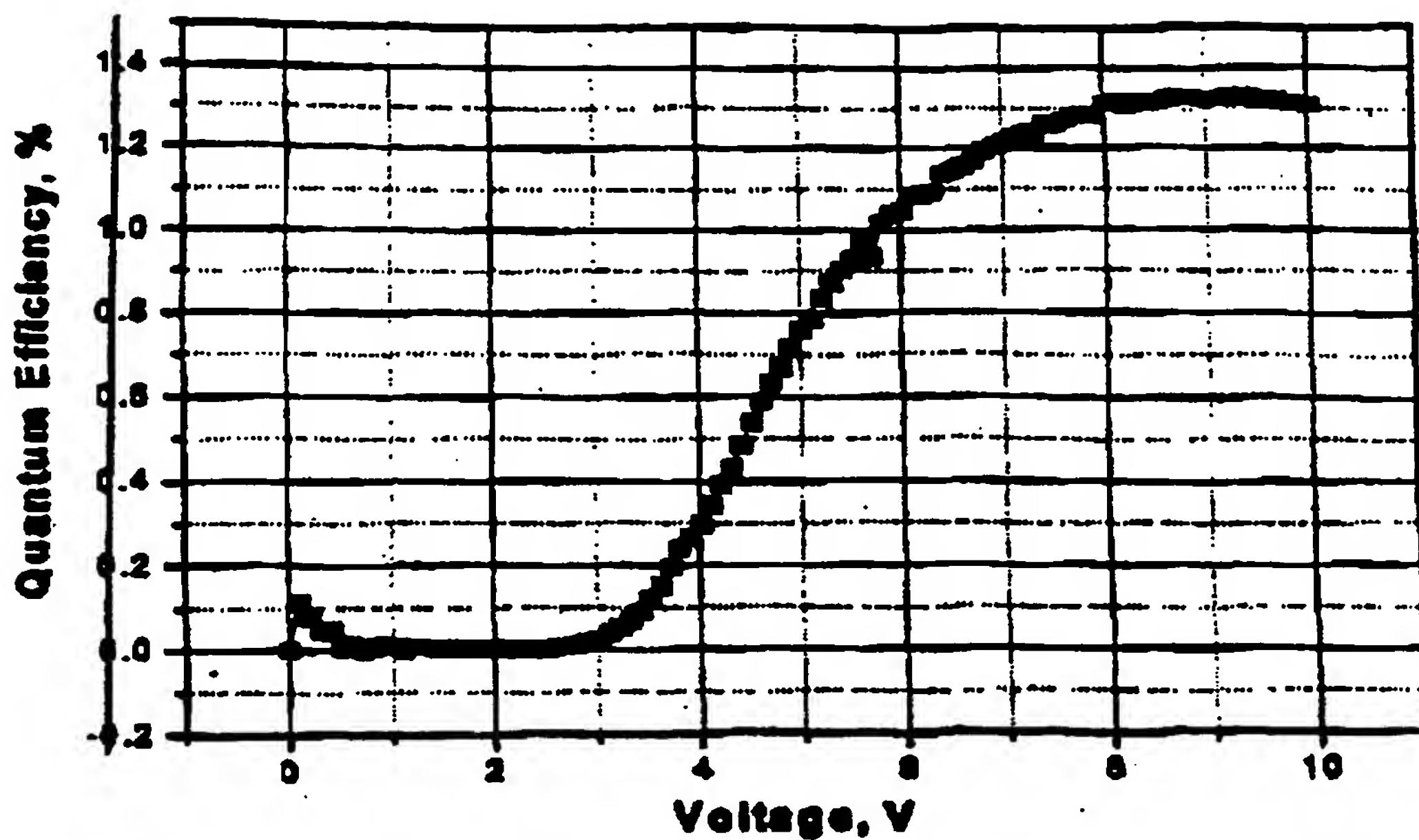
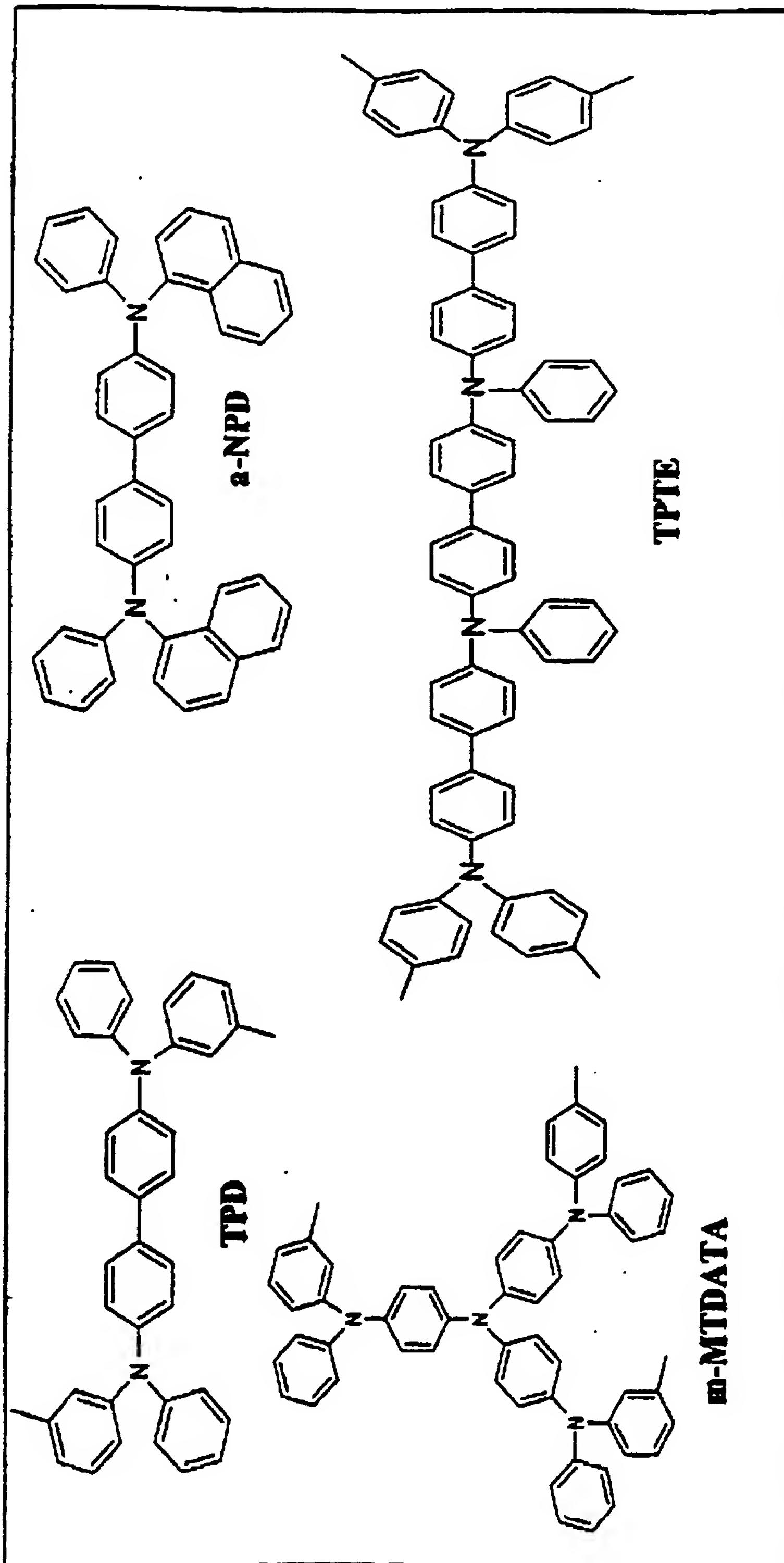


FIGURE 15

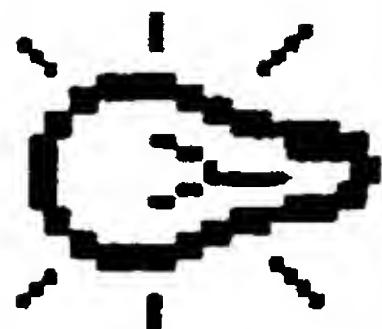


Conventional Hole-Transporting Materials used in OLEDs

FIGURE 16



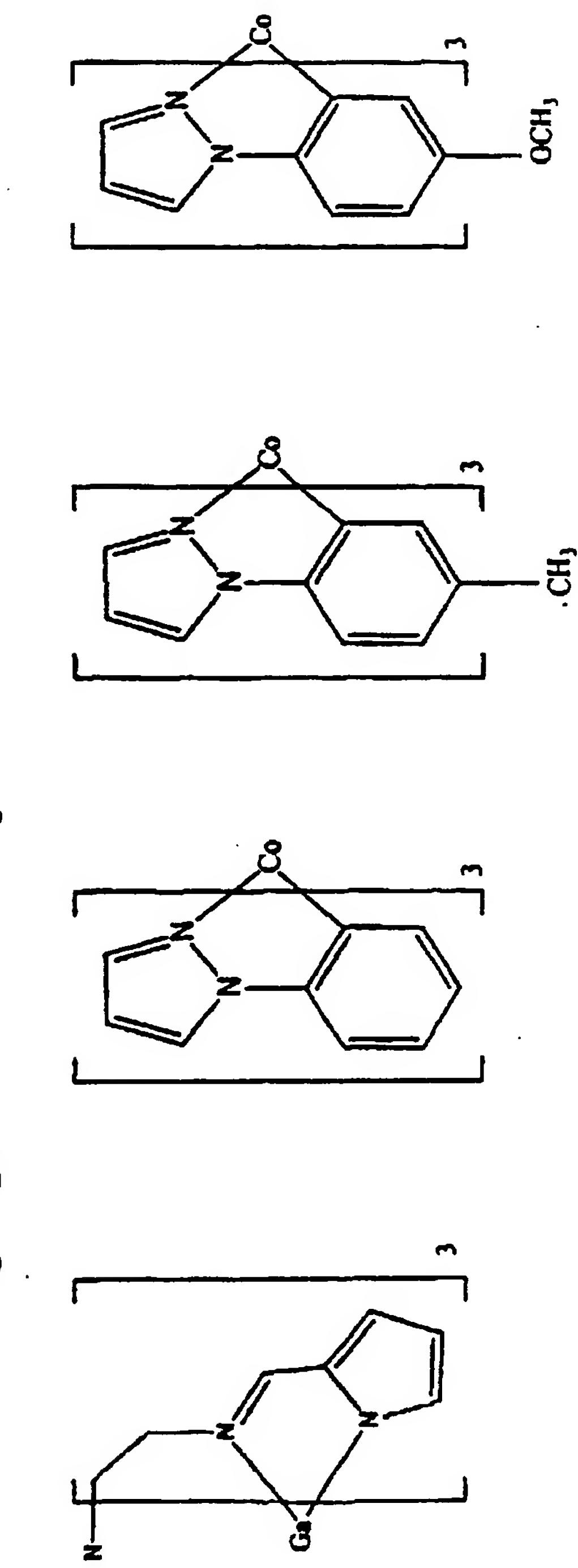
Triarylamine derivatives have proved to be excellent hole transporting materials for OLEDs. The hole mobilities in these materials are very high, due to the high degree of intermolecular π overlap and the planar nature of both the neutral and cationic forms of the molecules. The fact that both the neutral and cationic (hole) states for triarylamines leads to low reorganization energies and thus low barriers to electron transfer.



Organometallic Complexes may also be good candidates for charge transporting layers

Given the fact that metals have the ability to assume a variety of oxidation states, and the low kinetic barriers inherent in some organometallic self-exchange reactions.

FIGURE 17



Electron Self-Exchange Reactions (carrier migration)

- $A^+ + A \rightarrow A + A^+$, self exchange leads to carrier migration
- At the instant of electron transfer, the nuclei remain stationary, with no energy change in the system.
- Before electron transfer from one center to another can take place, the system must adjust so that the energy of the system is unaltered during electron transfer.
- The amount of distortion required to reach a common state is inversely related to the rate of electron transfer.

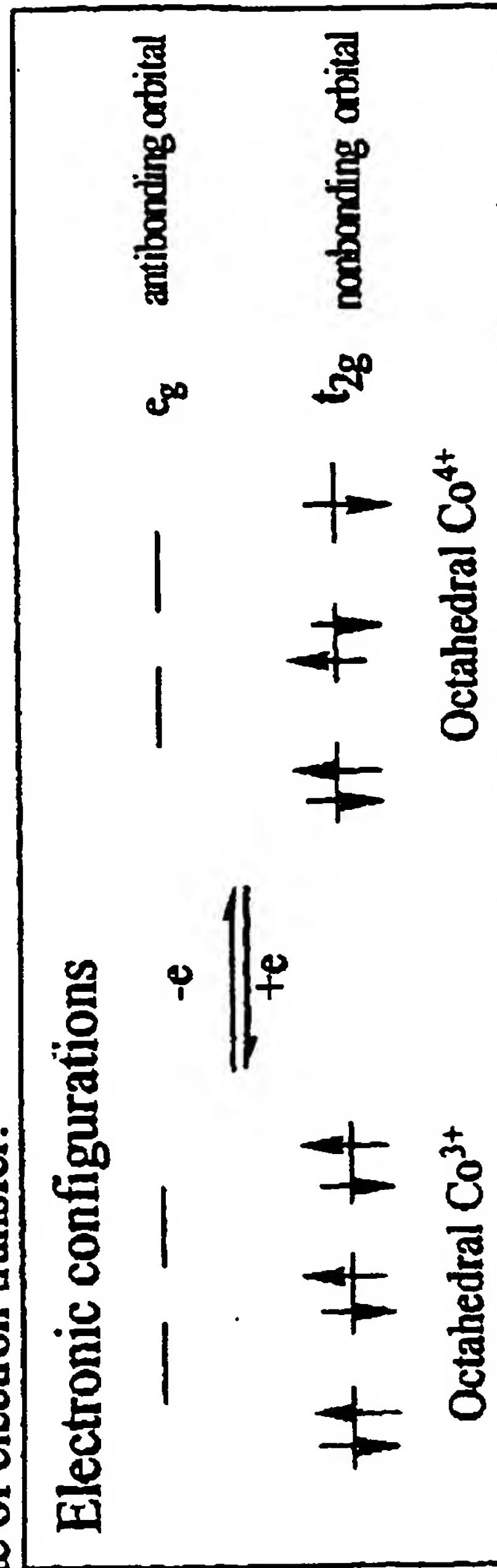
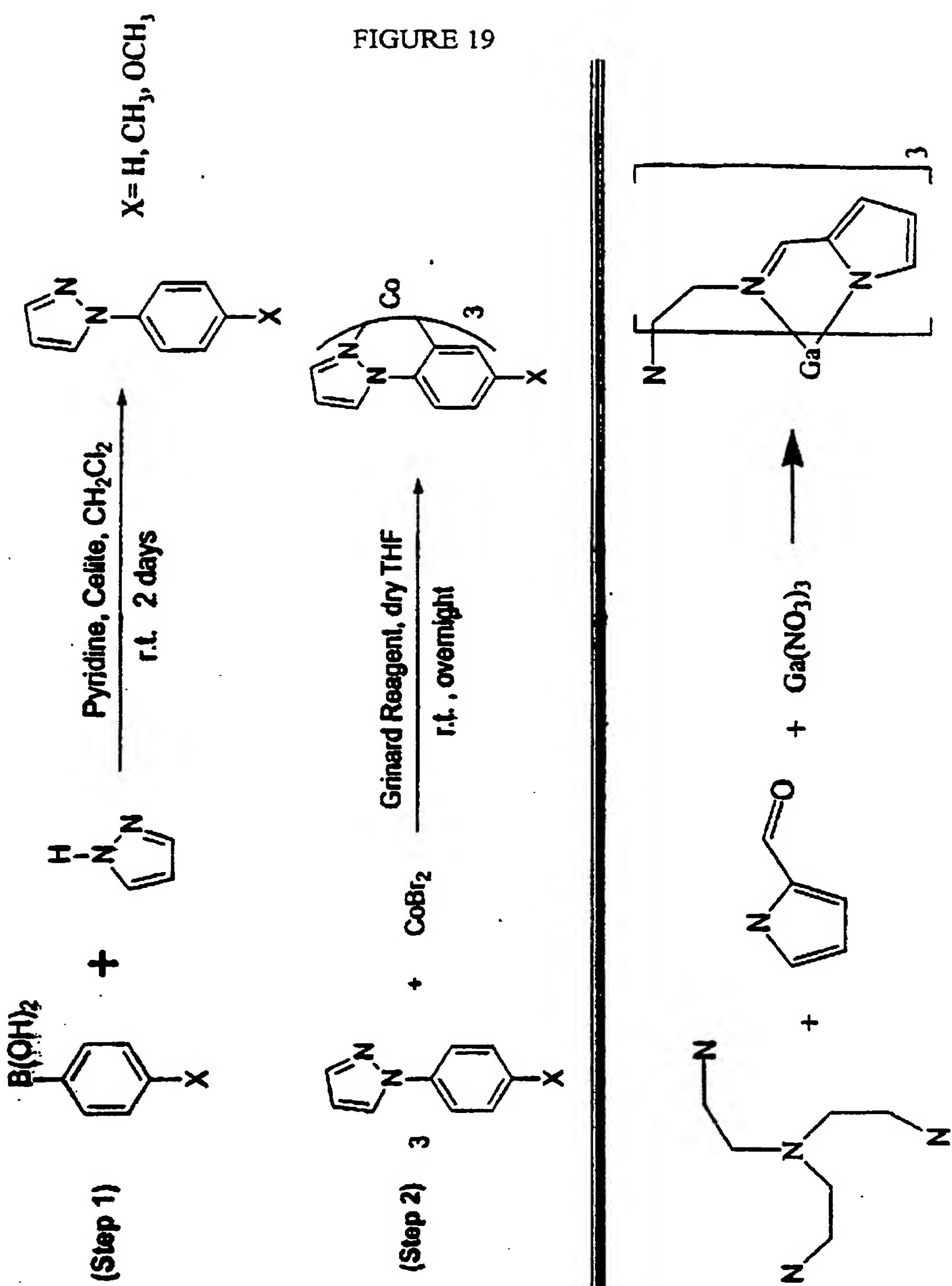


FIGURE 18

- Since t_{2g} is a nonbonding orbital, electrons into and out of this orbital involves small M-L changes.
- Since the two oxidation states have essentially the same structures, electron hopping between them may takes place with ease.

Synthesis of Cobalt (III) and Ga (III) Complexes

FIGURE 19



Absorption Spectrum

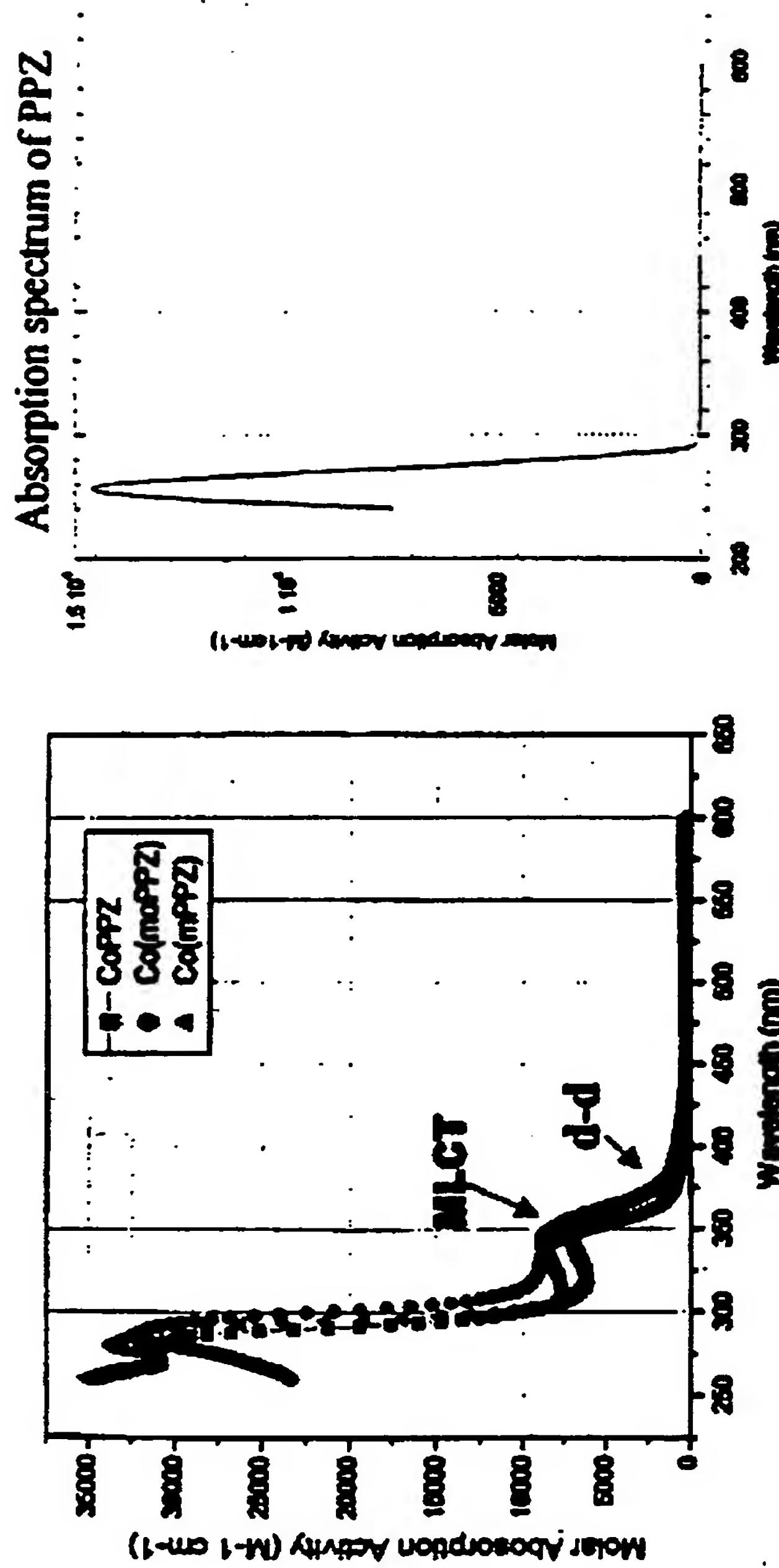
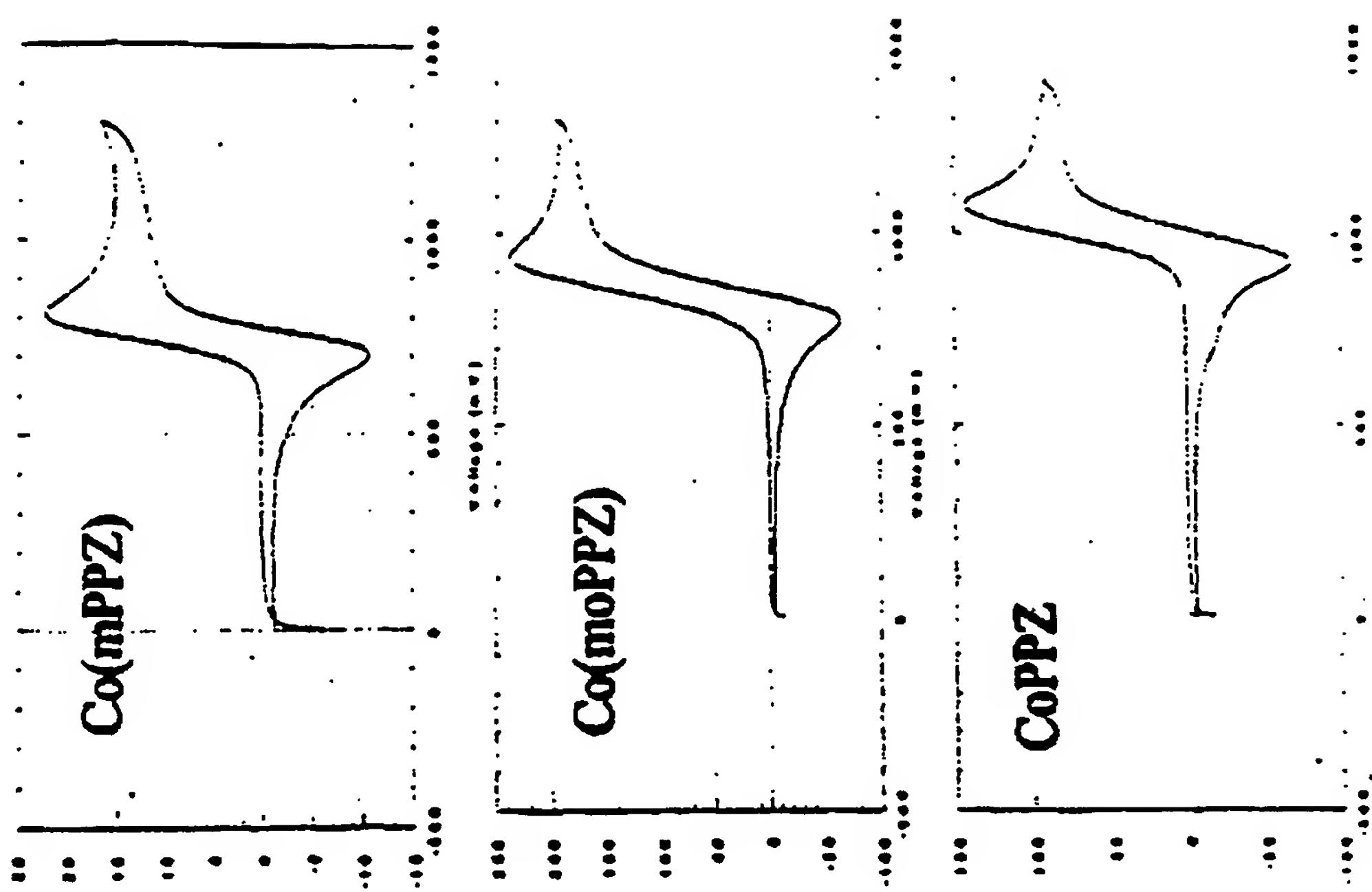


FIGURE 20

The intense peak below 300nm is assigned to the ligand-centered $\pi-\pi^*$ transition
 The broad, structureless band around 340nm is assigned to a metal-to-ligand charge transfer (MLCT) transition
 The broad shoulder in the low 400nm range corresponds to the $d-d$ transition, characteristic of octahedral Co^{3+} complexes

Cyclic Voltammetry and Ultraviolet Photoemission Data

FIGURE 21



The electron-rich phenylpyrazole ligand stabilizes the $\text{Co}(\square)$ species produced electrochemically.

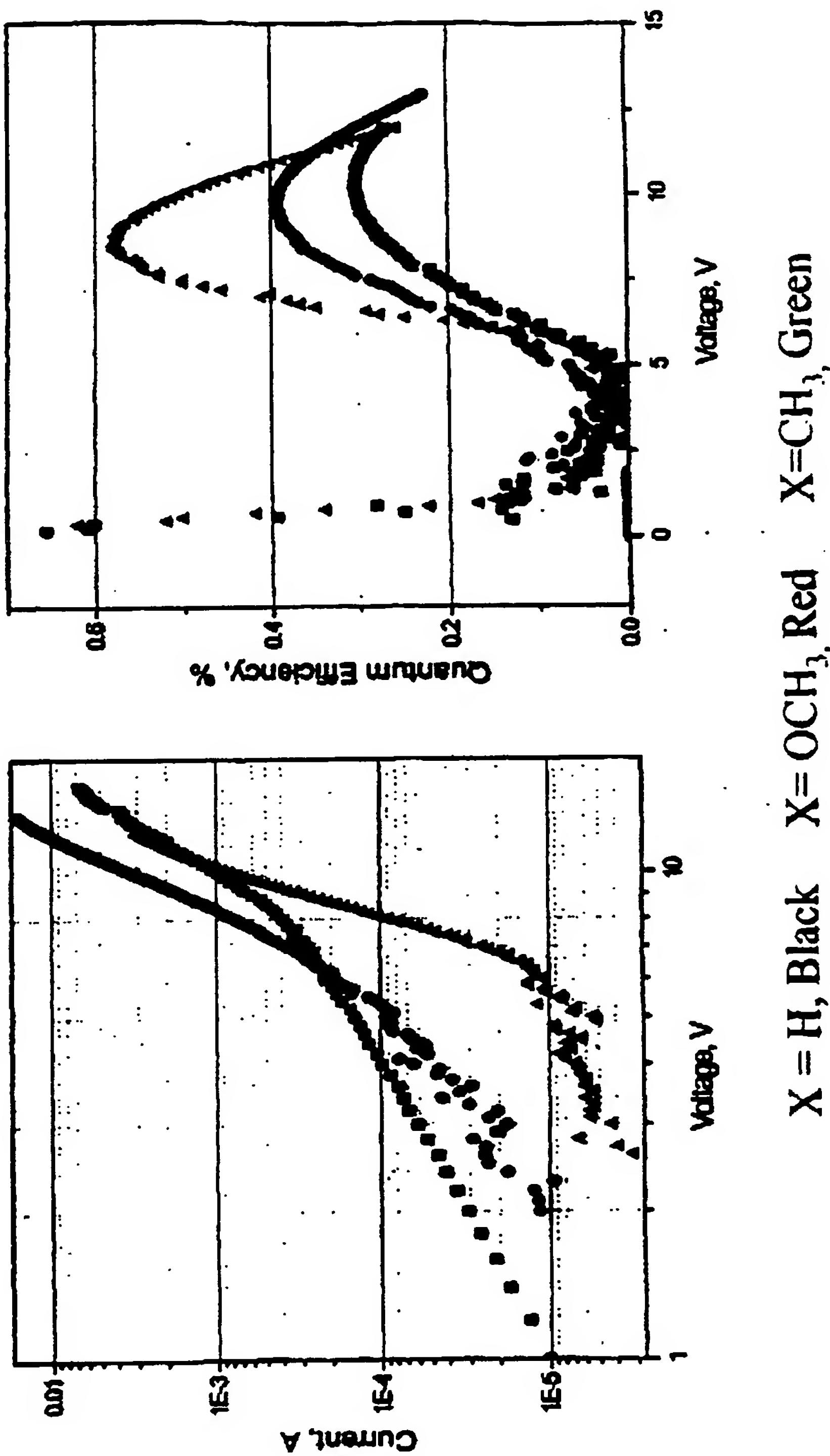
UPS Data (HOMO)

CoPPZ: 5.37eV
Co(mPPZ): 5.38eV
NPD: 5.51eV

Device incorporating Co(x PPZ) as the Hole Transporting Layer

Device Structure: ITO/Co(x PPZ)(250Å)/Alq(500Å)/Mg:Ag(1000Å)/Ag(400Å)

FIGURE 22



Introduction of a Thin NPD Layer as the Electron-Blocking Layer

ITO/CoPPZ(400Å)/NPD(100Å)/Alq(500Å)/Mg:Ag

FIGURE 23

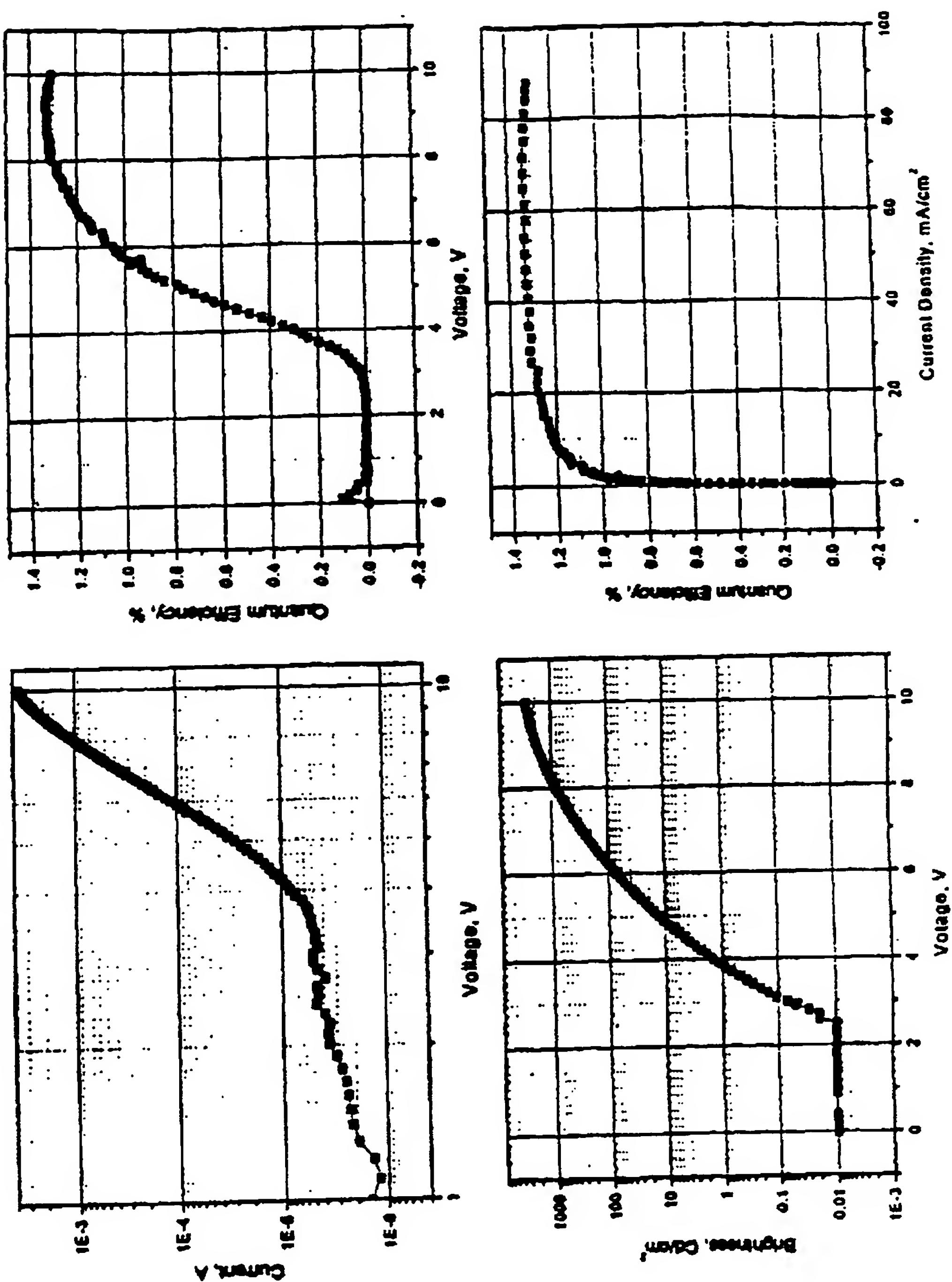
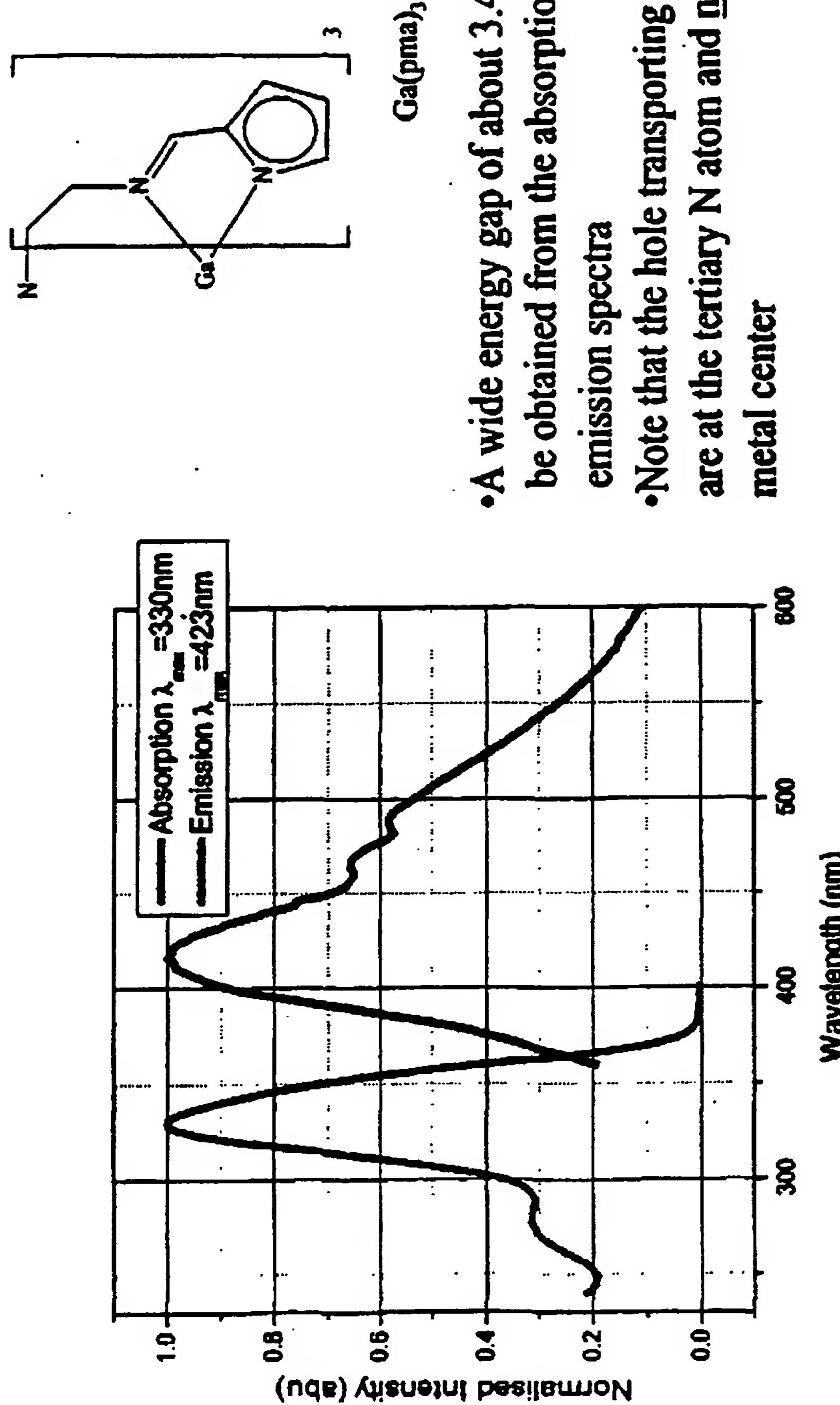


FIGURE 24

Photophysics of $\text{Ga}(\text{pma})_3$



The HOMO energy level, 5.74 eV (calculated using ultraviolet emission spectroscopy), and LUMO energy level, 2.34 eV, of $\text{Ga}(\text{pma})_3$ makes this compound energetically suitable as a hole transporting/electron blocking layer between CoPPZ and Alq.

(No electrochemistry of $\text{Ga}(\text{mpa})_3$ has been observed yet)

FIGURE 25

Efficient OLED with ONLY Metal Complexes(1)

ITO/Coppz(400Å)/GaPMAEA(100Å)/Alq(500Å)/Mg:Ag(1000Å)/Ag(400Å)

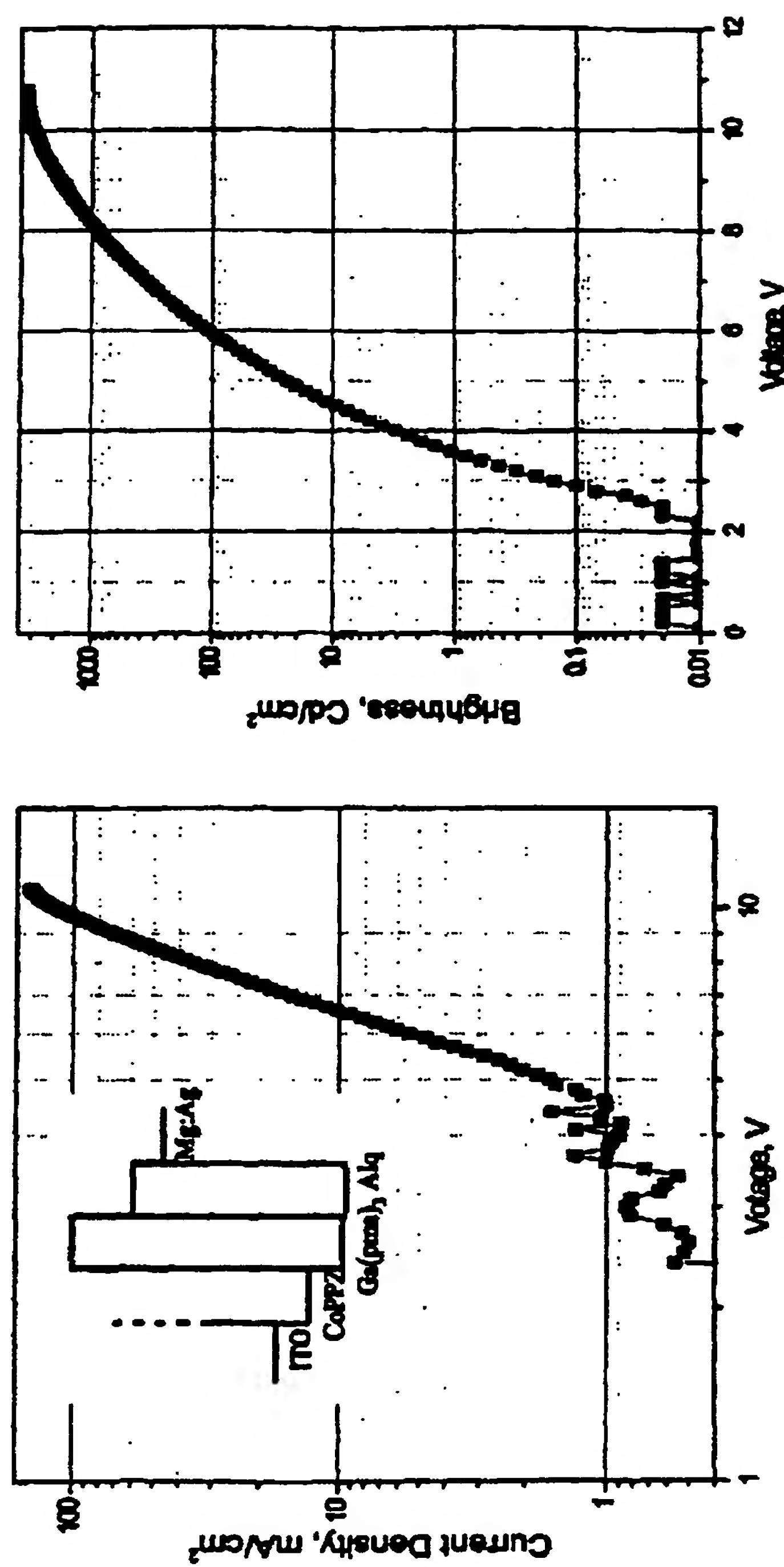
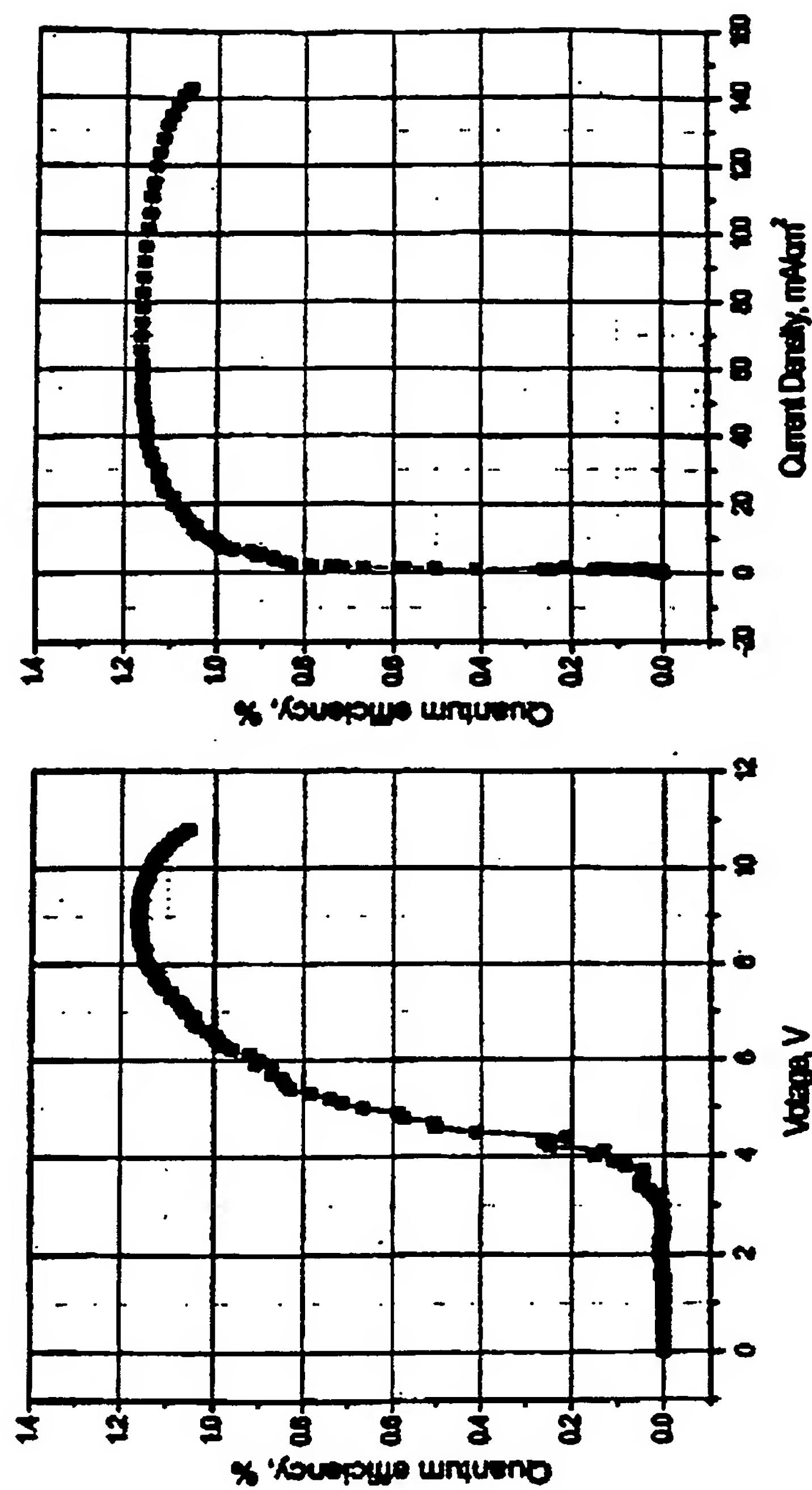


FIGURE 26

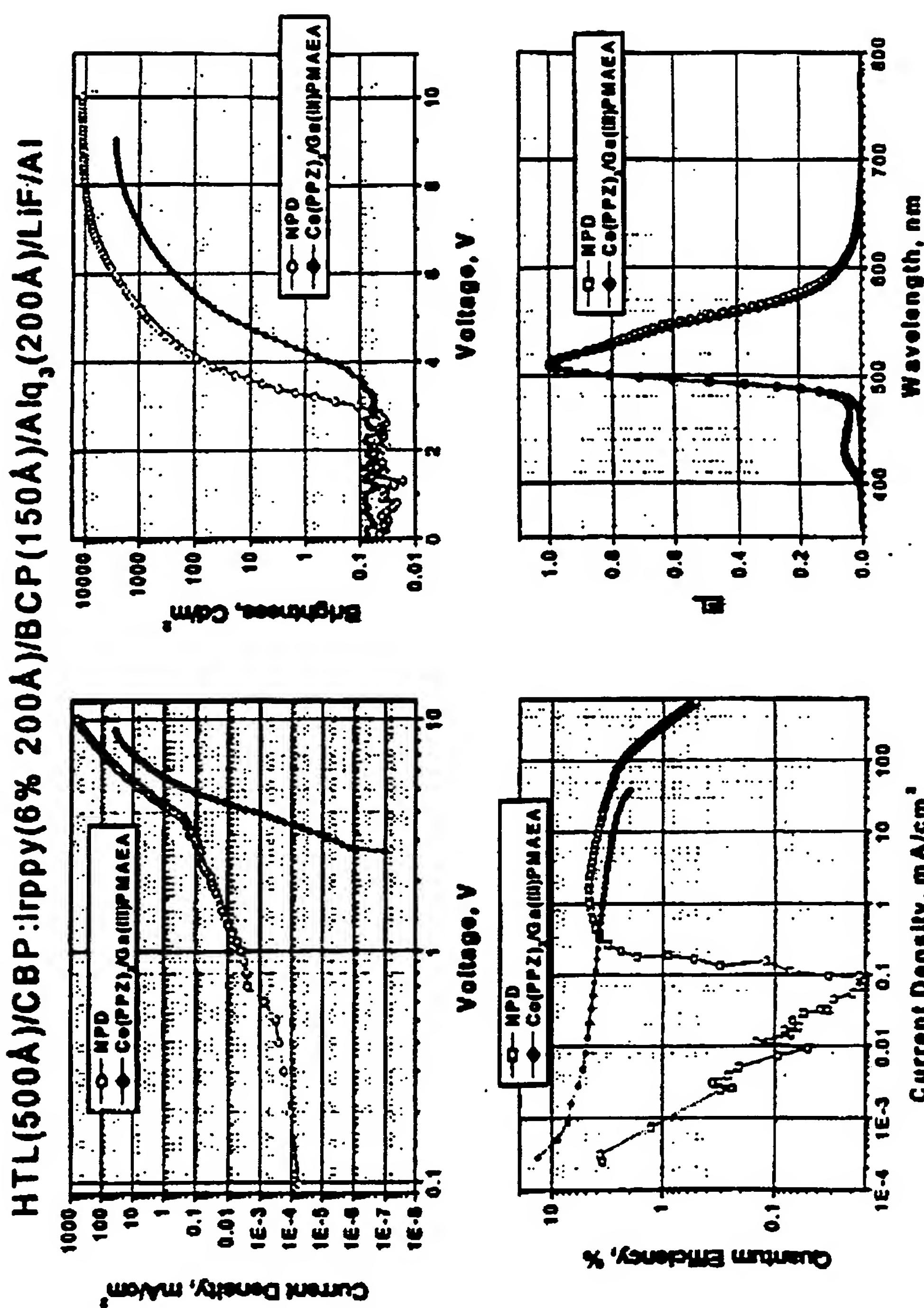
Efficient OLED with ONLY Metal Complexes(2)

ITO/Copper(400Å)/GaPMAEA(100Å)/Alq(500Å)/Mg:Ag(1000Å)/Ag(400Å)



Introduction of CoPPZ/Gapma into the phosphorescence devices

FIGURE 27



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/26820

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : H05B 33/00
US CL : 428/690, 917; 313/504

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 428/690, 917; 313/504

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P -- A, P	US 2002/0015860 A1 (MOTOMATSU et al) 07 February 2002 (07.02.2002), abstract, column 3, paragraph "0018", and entire patent.	1-8, 39-52, 59-68, 81, 82, 87, 88, 93 ----- 9-38, 53-58, 69-80, 83-86, 89-92
A	US 6,010,796 A (KIJIMA) 04 January 2000 (04.01.2000), entire patent.	1-93
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See patent family annex.

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Date of the actual completion of the international search

30 September 2002 (30.09.2002)

Date of mailing of the international search report

16 DEC 2002

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INTERNATIONAL SEARCH REPORT

PCT/US02/26820

Continuation of B. FIELDS SEARCHED Item 3:
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search terms: exciton, hole transporting, electron blocking layer, organometallic

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